

**Energy Research and Development Division  
FINAL PROJECT REPORT**

**DEMONSTRATION OF A NEW  
ELECTRODIALYSIS TECHNOLOGY  
TO REDUCE ENERGY REQUIRED FOR  
SALINITY MANAGEMENT**

Prepared for: California Energy Commission  
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## PREFACE

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## ABSTRACT

Managing the concentrate byproduct generated during desalination is becoming increasingly critical to the sustainable use of water and energy in California and much of the southwestern United States. The purpose of this project was to evaluate a new electro dialysis technology called electro dialysis metathesis, for treatment of reverse osmosis concentrate. The research team conducted testing with a full-size electro dialysis metathesis stack treating reverse osmosis concentrate from a desalination plant in Beverly Hills, California. The treatment goal for this process was to reduce reverse osmosis concentrate conductivity from 4.1 to 1.8 micro Siemens per centimeter. Electro dialysis metathesis successfully achieved this treatment goal while using only 0.6 kilowatt hours of energy per cubic meter of reverse osmosis concentrate treated (2.27 kilowatt hours per 1,000 gallons) and recovering 95 percent of the reverse osmosis concentrate as product water. The projected treatment cost using this method is \$2.30 per 1,000 gallons of reverse osmosis concentrate recovered as product water. The research team investigated treatment of the concentrate produced from this process for beneficial reuse with a two-step treatment process of chemical precipitation followed by electro dialysis with monovalent ion-selective membranes. The precipitation step yielded calcium carbonate, and the electro dialysis step yielded a sodium chloride-rich solution with the potential for reuse as the sodium chloride supply in the process. The research team concluded that electro dialysis metathesis holds promise for reducing the cost and energy requirements for concentrate treatment compared to existing methods, but further product development and commercial backing is needed to bring the technology to market. This project benefits California ratepayers because electro dialysis metathesis has the potential to address water supply, energy consumption, and salinity management issues across a wide range of municipal, agricultural, and industrial needs.

**Keywords:** Desalination, brine, concentrate, management, electro dialysis, electro dialysis metathesis, EDM,

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## EXECUTIVE SUMMARY

### Background

Water supply, energy consumption, and salinity management are critical issues in California that have become increasingly interdependent. Meeting the domestic and industrial water demands of a growing population will require municipalities to increase their reliance on alternative water sources such as brackish and reclaimed water.

Desalination with reverse osmosis (RO) membranes can be used to diversify and expand municipal water supplies, but desalination generates a liquid concentrate byproduct that must be managed to minimize environmental impact and avoid overload of the ability of conventional treatment plants to effectively treat conventional wastewater from sewer systems. The concentrate produced by the RO process is a mix of water and highly concentrated salt compounds and environmentally responsible management of this concentrate is a prerequisite to expanded use of brackish and recycled water.

For many inland communities, sustainable management of reverse osmosis concentrate will require zero liquid discharge (ZLD) desalination. In ZLD desalination, concentrate is treated to recover its water, and there is no discharge of liquid waste from a desalination plant. Sustainability is enhanced if the salts removed from concentrate can be used beneficially rather than being landfilled.

The established method for achieving ZLD desalination involves thermal desalination, but thermal desalination is expensive and energy intensive. Consequently, application of ZLD desalination has been inhibited by the cost and energy requirements of available methods. A new electrodialysis technology, electrodialysis metathesis (EDM), has emerged as an alternative to thermal desalination that offers the potential to reduce the costs and energy requirements for ZLD desalination.

The driving force in conventional electrodialysis (ED) is the electrochemical potential difference that exists between a positively charged anode and a negatively charged cathode. Conventional electrodialysis stacks contain repeating cell pairs, each of which is comprised of two compartments, a diluate compartment and a concentrate compartment, and two membranes, a cation selective membrane and an anion selective membrane. Each electrodialysis stack contains hundreds of repeating cell pairs between a cathode and anode. As water is pumped through the diluate compartment, anions and cations are transported through ion exchange membranes into the concentrate compartment and held there by electrostatic repulsion. The feed stream which enters the diluate compartment is demineralized, and all ions removed from this stream are then contained in the concentrate stream compartment. Recovery in membrane systems, whether reverse osmosis or electrodialysis, is limited by the precipitation potential of soluble salts in the concentrated stream; the primary factor determining scaling potential. EDM differs from conventional electrodialysis by its unique arrangement of membranes and use of sodium chloride (NaCl). Rather than a cell pair, the EDM repeating unit, referred to as a quad, comprises four compartments and four membranes. Each EDM quad contains one diluate, one sodium chloride, and two concentrate compartments. This arrangement causes ions in the EDM

feed to be separated into two highly soluble concentrate streams, one containing mostly chloride with cations and the other containing mostly sodium with anions. The least soluble salt in EDM concentrate, sodium bicarbonate, is over 40 times more soluble than calcium sulfate, a salt that commonly limits recovery during desalination with ED or RO. Consequently, scaling by low solubility salts is avoided, and EDM is capable of treating reverse osmosis concentrate streams to recover up to 95 percent of these streams as product water.

## **Purpose**

The goal of this project was to evaluate the technical and economic feasibility of using EDM to treat RO concentrate generated at a brackish water desalination facility. The research team tested a full-scale EDM stack with reverse osmosis concentrate generated at the Beverly Hills Water Treatment Facility (BHWTF).

## **Objectives**

The objective was to optimize EDM treatment and assess full-scale treatment costs for each testing site.

Specific project objectives were to evaluate the following key parameters of EDM performance:

- EDM energy requirements
- Resistance across the EDM stack
- EDM stack current utilization efficiency
- Limiting current density for the EDM system
- EDM separation of ions into two high-solubility concentrate streams
- Water recovery achievable with EDM
- Rate of water transport through the EDM membranes
- Relative transport of ions through the EDM membranes
- Viability of treating EDM concentrate to recover sodium chloride and other salts
- Strategies for optimizing EDM energy and treatment cost for different concentrate water qualities

The research team used results from BHWTF concentrate treatment testing to evaluate treatment of RO concentrate with EDM at three sites in California: the Beverly Hills Water Treatment Facility, the Arcadia Water Treatment Plant in Santa Monica, and the Santa Rosa Water Reclamation Facility operated by the Rancho County Water District. The objective was to optimize EDM treatment and assess full-scale treatment cost for each site.

## **Benefit to California Ratepayers**

There may be no region in the world where the interrelated and often competing challenges of water supply, energy consumption, and salinity management are more critical than in California. The ability to efficiently manage concentrate liquid streams resulting from

desalination, agricultural runoff, power plant cooling water, and industry is at the core of all of these issues. This project will benefit Californians because with additional research and demonstration EDM has potential to help achieve near-zero liquid discharge associated with RO water recovery with lower energy consumption than thermal water treatment which is the current method of achieving ZLD associated with water recovery for beneficial reuse.

## Conclusions

The following are conclusions based on field test results and desktop evaluations:

- EDM successfully treated the Beverly Hills facility's RO concentrate with an energy consumption of approximately 0.6 kilowatt hours (kWh) per cubic meter (m<sup>3</sup>) of RO concentrate treated (2.27 kWh per 1,000 gallons) while recovering 95 percent of the RO concentrate as product water.
- If applied at full-scale for all the plant's concentrate, recovery of 95 percent of RO concentrate as water by EDM would increase the total plant recovery at the BHWTF from 74 percent to 99 percent
- EDM concentrate was treated in a two-step process of precipitation followed by electrodialysis to produce calcium carbonate solids and a sodium chloride-rich stream with potential for reuse in the EDM process as the NaCl supply.
- We projected full-scale EDM costs for the three study sites. The EDM treatment cost included the capital cost for installation of EDM equipment and the operating costs for EDM energy and sodium chloride consumption. Treatment costs for the three concentrate streams evaluated ranged from \$2.30 to \$4.50 per 1,000 gallons of RO concentrate treated.
- The research team assessed the market readiness of the EDM based on the study results. We concluded that the technology offers potential to reduce the costs and energy requirements for concentrate treatment as an alternative to thermal processes, but at the time of the report, EDM lacked commercial backing to further develop the technology and bring it to market.
- EDM performance and treatment cost depends on site-specific water quality and treatment goals. We recommend that any utility interested in exploring EDM for concentrate management conduct on-site testing to determine costs and energy requirements and to understand operating requirements.

# CHAPTER 1:

## Introduction

### 1.1 Project Objective

Water supply, energy consumption, and salinity management are critical issues in California that have become increasingly interdependent. Meeting the domestic and industrial water demands of a growing populace will require municipalities to increase their reliance on alternative water sources such as brackish and reclaimed water.

Desalination can be used to diversify and expand municipal water supply portfolios, but desalination generates a concentrate byproduct that must be managed. Discharging concentrate to an inland water body or a wastewater treatment plant merely transfers salt to another watershed or recycles it within the same watershed without providing a sustainable salinity management solution.

Expanded use of brackish and recycled water will increase the importance of developing sustainable salinity management solutions. California is home to some of the most productive agricultural fields in the world, but increasing soil salinity is threatening continued agricultural use of large tracts of land in regions like the West San Joaquin Valley.

One method for managing salinity is to treat desalination concentrate to recover it as product water through ZLD desalination which conserves water and retains salt in solid form thereby removing it from the water cycle. This method, however, requires an energy-intensive thermal process. The expense and energy requirements of existing methods, however, inhibit the use of ZLD desalination.

Recently a new electrodialysis (ED) technology, electrodialysis metathesis (EDM), was demonstrated at pilot scale to reduce ZLD cost and energy consumption relative to thermal treatment for slightly brackish to moderately brackish water sources (Bond et al., 2011). EDM holds promise to help optimize efficiency of water and energy use associated with desalination, water reclamation, and agricultural production in California.

Reducing the cost and carbon footprint required to recover product water from concentrate is a requisite first step toward sustainable inland desalination; but to be truly sustainable inland desalination must also include management of the solid byproducts. To illustrate, a 10 million gallon per day (mgd) desalination facility treating brackish water containing 2,000 milligrams per liter (mg/L) of total dissolved solids (TDS) at 80 percent recovery will generate 83 tons of salts each day in its concentrate stream.

Managing the salt byproducts in concentrate remains a critical challenge in the quest for sustainable inland desalination. Landfill disposal of vast salt volumes is neither economical nor environmentally sustainable, and doing so seems particularly wasteful when the salts generated during desalination have potential commercial value. The challenge in commercializing these



salts is finding effective methods for separating the mixture of salts contained in concentrate into individual salts of sufficient purity for commercial use.

There are unique features of the EDM treatment process that enhance the potential to develop salt products from desalination concentrate streams. Therefore, EDM has the potential to meet both criteria for sustainable inland desalination: reduction in the cost and energy consumption for water recovery and development of salt products from concentrate dissolved solids.

To evaluate this technology, the research team operated a full-size EDM stack to treat reverse osmosis (RO) concentrate generated at the Beverly Hills Water Treatment Facility (BHWTF). The overall project goal was to assess the viability of EDM for reducing the energy and cost required to treat concentrated water streams. The solution investigated in this project has potential to treat concentrate from desalting treatment plants, water reclamation facilities, agricultural runoff, and power plant cooling water.

Specific project objectives were to investigate the following key parameters of the EDM process during treatment of RO concentrate at the BHWTF:

- EDM energy requirements
- Resistance across the EDM stack
- EDM stack current utilization efficiency
- Limiting current density for the EDM system
- EDM separation of feed ions into two concentrate streams of high solubility
- Water recovery achievable with EDM
- Rate of water transport with ions through EDM membranes
- Relative transport of ions through the EDM membranes.
- Treatment of EDM concentrate to recover sodium chloride and other salts.
- Optimal strategy for using EDM to reduce energy requirements and minimizes waste byproducts

## **1.2 Background**

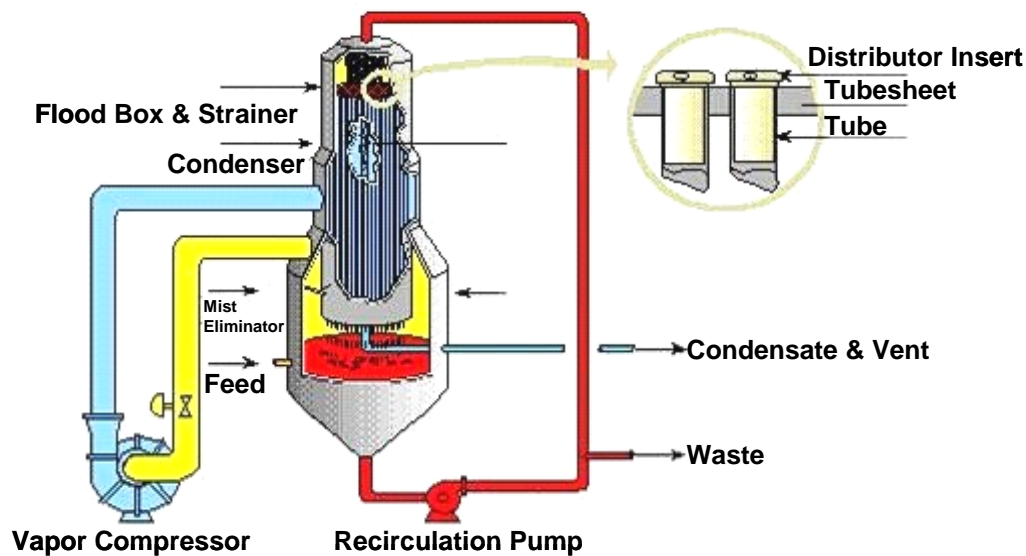
### **1.2.1 Established Method of ZLD Desalination**

The established method for achieving ZLD desalination is thermal desalination, typically with brine concentrator followed by a crystallizer. Thermal processes have been used for decades to desalinate water, particularly in the Middle East where energy has been relatively inexpensive. Thermal desalination is accomplished by evaporating water, condensing the resulting steam, and recovering the condensate as high quality product water.

The mechanical vapor compression (MVC) brine concentrator is shown schematically in Figure 1.1. The brine concentrator is a falling film evaporator with a sump at the bottom of its column

and condensation tubes extending vertically above the sump. Feed water is heated and discharged to the sump. Vapor above the sump is drawn off and compressed in a vapor compressor. Heated water in the bottom of the sump is pumped to the top of the condensate tubes and allowed to fall down the inside of the tubes. Compressed vapor is discharged to the outside of the condensate tubes. The temperature of the compressed vapor is greater than that of the water inside the tubes, and heat exchange between the vapor and the water inside the tubes causes the vapor to condense on the outside of the tubes. This condensate is captured as product water.

**Figure 1.1: Thermal brine concentrator schematic**



Recovery of feed water in the brine concentrators depends on water quality, and recoveries between 90 and 95 percent are typical. Concentrations of TDS in the brine concentrator can reach 250,000 mg/L. Many brine concentrators used a seeded slurry feed to reduce the potential for scaling. Calcium sulfate and calcium carbonate scales that would attach to heat transfer surfaces instead attach to calcium sulfate seeds in the slurry allowing higher recovery in the brine concentrator.

A percentage of the water in the brine concentrator sump is bled off to maintain TDS concentrations below levels where scaling by salts would occur. If ZLD desalination is required, the bleed discharge from the brine concentrator, typically 5 to 10 percent of the feed water, can be treated in a second thermal desalination device, the crystallizer.

The crystallizer is similar to the brine concentrator. The primary difference between the two is that in the crystallizer brine is pumped under pressure up through the condensation tubes rather than falling down the tubes by gravity. This is to maintain a higher flow velocity in the

tubes to inhibit scale formation. A waste stream is drawn off to a filter press for liquid/solid separation.

When the brine concentrator and crystallizer are used in series, virtually all of the water is recovered as product water. The product water from each process is a high quality distillate with TDS typically less than 10 mg/L.

These thermal devices are energy intensive with typical energy requirements of 20 kWh/ m<sup>3</sup> treated for a brine concentrator and 80 kWh/m<sup>3</sup> treated for a crystallizer. To put these figures in context, the energy required to desalinate brackish water with RO membranes is around 0.5 kWh/ m<sup>3</sup>. The equipment is also very expensive due to the specialty materials required to withstand corrosion. Treatment cost, including amortized capital cost and operating cost to treat concentrate from a brackish water desalination facility is typically greater than \$3.30 per cubic meter of concentrate treated (\$12 per 1,000 gallons) (Bond and Veerapaneni 2007). Given the cost and energy required for thermal desalination, increasing product water recovery with membrane separation processes and thereby reducing the volume of concentrate treated with thermal technologies is a promising strategy for reducing the treatment cost and energy consumption for concentrate management.

Recovery in membrane separation processes, such as RO, ED, and electrodialysis reversal (EDR) is limited by the membrane fouling potential of precipitates of sparingly soluble salts. Common precipitates of concern during brackish water desalination include calcium carbonate (CaCO<sub>3</sub>), calcium sulfate (CaSO<sub>4</sub>), and silica (SiO<sub>2</sub>).

### 1.2.2 Fundamentals of Electrodialysis and EDM

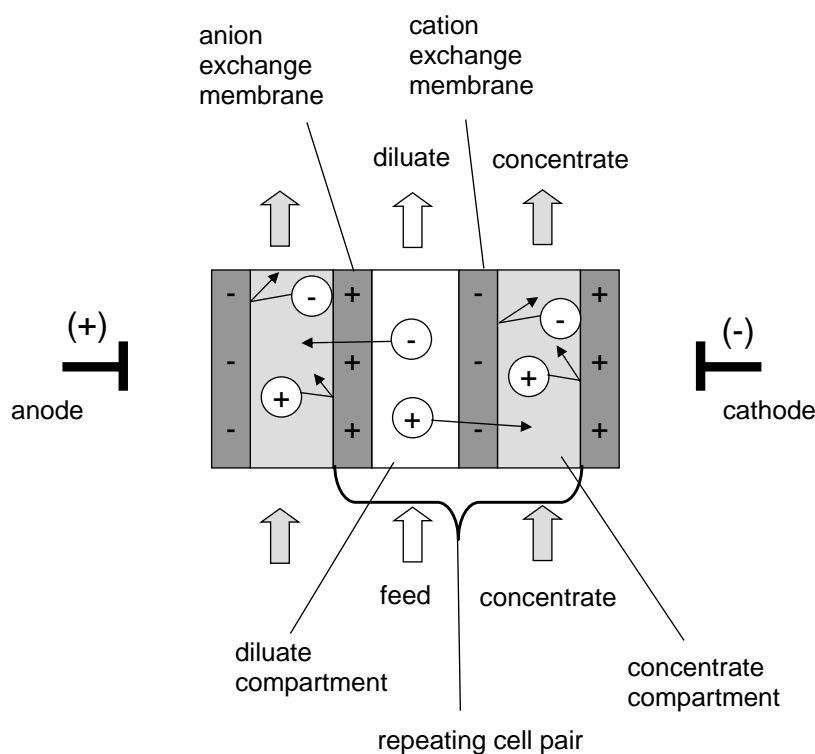
EDM is designed to circumvent recovery limitation through a unique arrangement of electrodialysis compartments that separates the feed salts into two concentrate streams of highly soluble salts. This concept is best described by noting the differences between EDM and conventional electrodialysis.

The conventional ED process is shown schematically in Figure 1.2. The driving force for ED is the electrochemical potential difference between a positively charged anode and a negatively charged cathode. A typical ED stack contains hundreds of repeating cell pairs between a cathode and anode, each containing a cation and an anion exchange membrane, a diluate compartment, and a concentrate compartment. As water is pumped through the diluate compartment, anions and cations are transported through ion exchange membranes into the concentrate compartment and held there by electrostatic repulsion from same charge ion exchange membranes. The diluate stream is thus demineralized, and all ions removed from diluate are contained in the concentrate stream. Recovery in ED is limited by the precipitation potential of sparingly soluble salts in the concentrate compartments in the same manner recovery is limited during desalination with RO membranes.

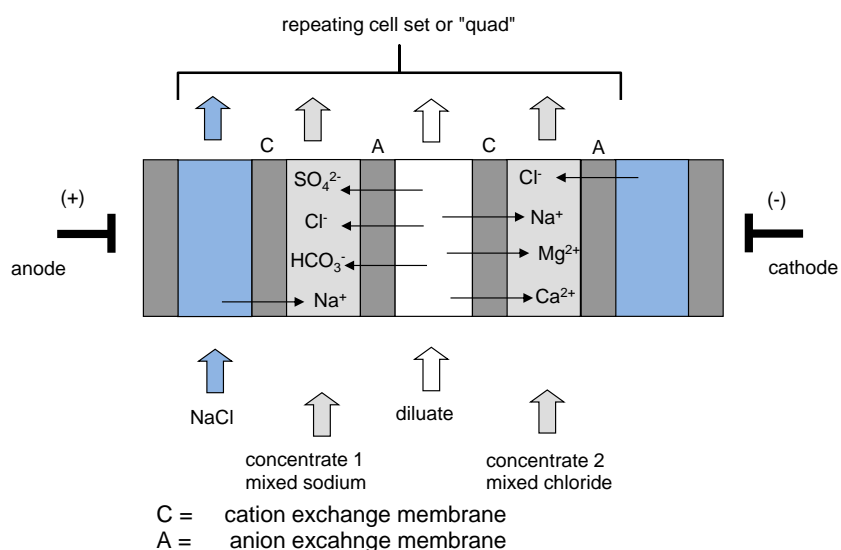
A schematic of EDM is shown in Figure 1.3. Rather than a cell pair, the EDM repeating unit comprises four compartments and four membranes. The compartments are arranged so each diluate compartment is between two concentrate compartments and each concentrate compartment is between a diluate compartment and a sodium chloride compartment.

Anions are transported through anion exchange membranes from the diluate into the compartment containing concentrate 1 while sodium from the sodium chloride compartment is transported through cation exchange membranes into concentrate 1. Concentrate 1 is referred to as the mixed sodium concentrate stream because it contains mostly sodium with anions. Similarly, cations are transported from the diluate stream into concentrate 2 while chloride is transported from the sodium chloride compartment into concentrate 2. Concentrate 2 is referred to as the mixed chloride concentrate because it contains mostly chloride and cations. The result is separation of ions into two streams of highly soluble salts because divalent cations and divalent anions are not present in either stream at sufficient concentration to cause precipitation of low solubility salts such as calcium sulfate and calcium carbonate.

**Figure 1.2: Conventional Electrodialysis Schematic**

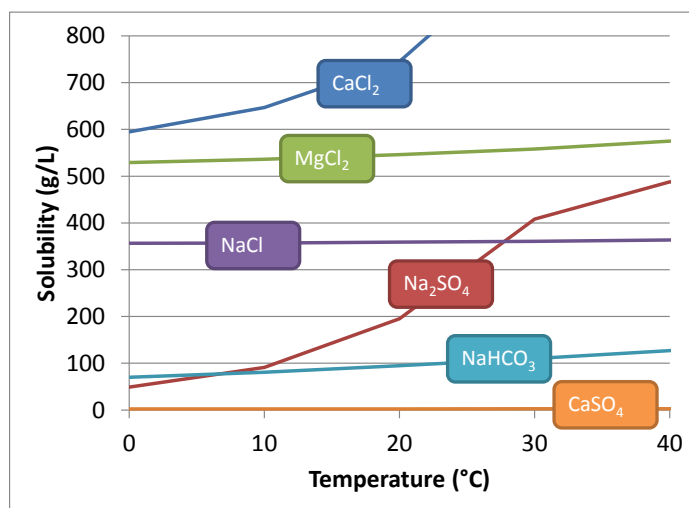


**Figure 1.3: Electrodialysis Metathesis Schematic**



The significance of EDM concentrate separation into two streams is illustrated in Figure 1.3. The solubilities of salts with potential to form in EDM, sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), calcium chloride ( $\text{CaCl}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ), and sodium chloride ( $\text{NaCl}$ ), are compared to the solubility of calcium sulfate, a major scalant of concern in RO and other desalination systems. As illustrated in Figure 1.4, at 25 degrees Centigrade ( $^{\circ}\text{C}$ ), the least soluble of the potential EDM scalants,  $\text{NaHCO}_3$ , is 40 times more soluble than  $\text{CaSO}_4$ . Consequently, EDM can be operated at much higher recovery than RO, ED, or EDR without risk of membrane scaling.

**Figure 1.4: Solubility of Salts Produced by EDM Compared with Solubility of Calcium Sulfate ( $\text{CaSO}_4$ )**



Where recovery in electrodialysis is not governed by precipitation potential of salts, it is determined by the amount of water transported across the membranes into the concentrate compartments. Water transport from diluate to concentrate compartments occurs during electrodialysis by two mechanisms: 1) electroosmosis, the transport of water molecules associated with ions, and 2) osmosis driven by the concentration difference between the diluate and concentrate streams. Transport by osmosis increases with as osmotic pressure increases. Equations used to describe the behavior of electrodialysis have been in use for decades, and electrodialysis theory is well understood. Current is carried in electrodialysis by the migration of ions. By Faraday's Law, the current,  $I$  (A), required for the transfer of a given quantity of ions is proportional to Faraday's constant,  $F$  (96,485 A·s eq<sup>-1</sup>), diluate flow,  $q$  (L s<sup>-1</sup>), concentration of ions transferred,  $\Delta N$  (eq L<sup>-1</sup>), and the reciprocal of the current utilization factor,  $\zeta$ .

$$I = \frac{Fq\Delta N}{\zeta}$$

The current utilization factor expresses the electrical efficiency of the stack. It is the ratio of actual equivalents transferred to the theoretical number of equivalents that would be transferred by Faraday's Law with ideal membranes and no electrical short-circuiting. Generally, industrial electrodialysis stacks have current utilization factors between 70 and 90 percent.

$$\zeta = \frac{\Delta N_{observed}}{\Delta N_{theoretical}}$$

Current density,  $i$  (A/cm<sup>2</sup>), is the current divided by membrane area,  $A_m$  (cm<sup>2</sup>).

$$i = \frac{I}{A_m}$$

Current is related to applied voltage by Ohm's law, where  $U$  is the difference in electric potential in volts, and  $R$  is resistance in ohms.

$$U = I R$$

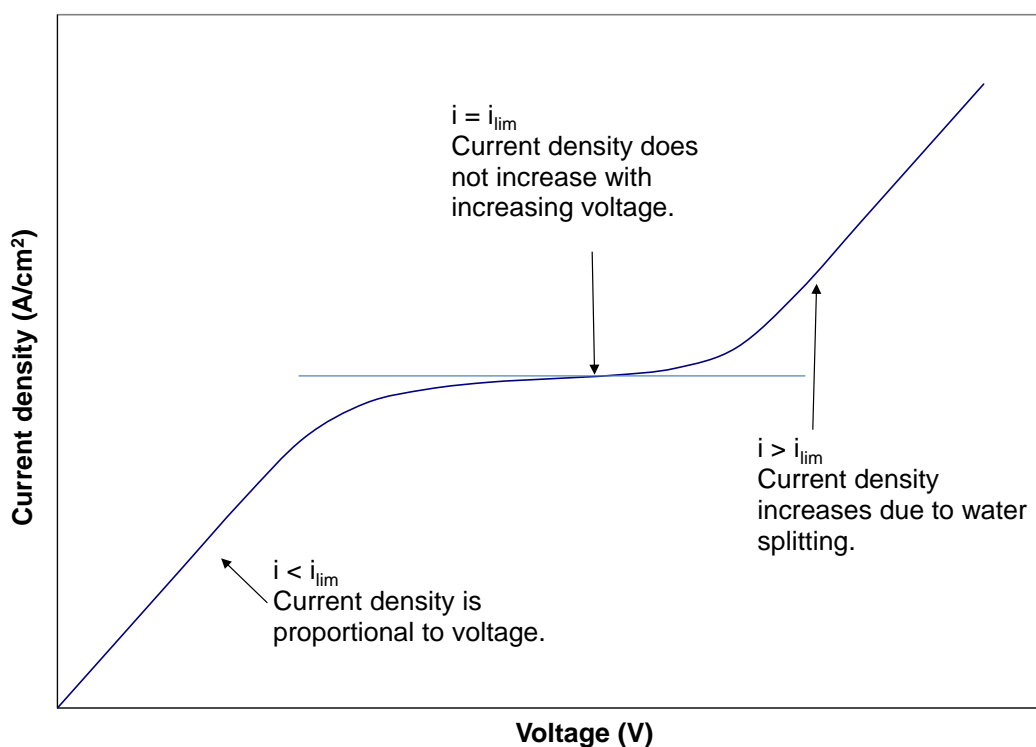
The resistance of an EDM cell set is the sum of the resistances in the diluate compartment, the concentrate compartments, the sodium chloride compartment, and the four membranes.

Because current in electrolyte solutions is carried by ions, a limiting current density ( $i_{lim}$ ) is reached when the concentration of ions available to transfer current approaches zero in the diffusion boundary layer on the feed side of the membrane. At the limiting current density, increases in voltage do not increase current density until voltage is high enough to split water molecules into H<sup>+</sup> and OH<sup>-</sup>. After water splitting occurs, current is carried by H<sup>+</sup> and OH<sup>-</sup> ions, and current again increases with voltage. Operation near the limiting current density must be avoided because pH extremes caused by water splitting can damage the membranes and cause precipitation of pH sensitive salts.

The concept of limiting current density is illustrated in Figure 1.5. The graph depicts current density as voltage is steadily increased. Initially, current density increases in proportion to the increase in voltage, indicating that current is not limited by the concentration of ions in the membrane boundary layer. As ions are depleted in the boundary layer, a point is reached where increase in voltage no longer produces a proportional increase in current, and the graph becomes curvilinear. The limiting current density is reached where current density does not increase with increased voltage due to resistance across the ion-depleted diffusion boundary layer. Beyond the limiting current density, current again increases as voltage increases because water is split and current is carried by  $H^+$  and  $OH^-$  ions.

The value of the limiting current density depends on the concentration of ions in the water, cell geometry, and hydrodynamic conditions in the ED channels between membranes. ED membranes are separated by a mesh spacer, and the width of the spacer determines the channel width. Limiting current density increases as the concentration of ions in the water increases and as the thickness of the membrane boundary layer decreases. The thickness of the boundary layer is affected by channel velocity and the geometry of the spacer. As velocity increases, flow becomes more turbulent causing a decrease in the boundary layer thickness and an increase in limiting current density. Increasing flow velocity, however, also reduces the residence time through the stack and the time available for ion transfer.

**Figure 1.5: Electrodialysis Limiting Current Density**



It is difficult to measure the boundary layer thickness, but the ratio of current density to the log mean normality ( $N_m$ ) in the diluate stream (eq/L) has been observed to be constant for a given boundary layer thickness (Lee, Oh, and Moon 2002). This ratio is referred to as the polarization parameter (PP) and the units are A · cm/eq. The value of PP at  $i_{lim}$  is referred to as the limiting polarization parameter,  $PP_{lim}$ .

$$PP_{lim} = \frac{i_{lim}}{N_m}$$

The relationship between  $PP_{lim}$  and cell velocity for common spacer types was evaluated by Davis and Lacey (1970), and their results are presented here as Figure 1.6 to illustrate the effect of temperature and cell velocity on limiting polarization parameter. They found  $PP_{lim}$  to be a power function of cell velocity (note  $v$  rather than  $U$  is used in this report for cell velocity).

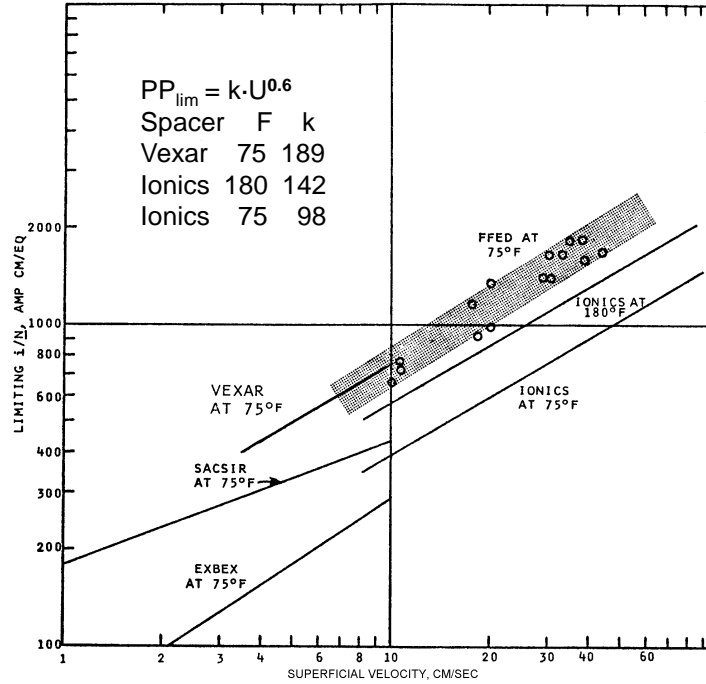
Electrical resistance increases as salt concentrations in the diluate decrease, and consequently greater voltage is required to maintain a constant current. The voltage that can be effectively applied to an individual stack is constrained by the limiting current density.

The concept of limiting polarization parameter provides a powerful tool for evaluating electrodialysis. Theoretically, once the specific conductivity ( $k$ ) and ion activity ( $a$ ) constants are determined for a spacer configuration at a specific temperature, the limiting polarization parameter, and hence limiting current density, can be estimated for a given water composition over a wide range of cell velocity at that temperature.

$$PP_{lim} = k v^a$$



**Figure 1.6: Limiting Polarization Parameter of Different Membrane Spacers (Davis and Lacey, 1970)**



The effectiveness of a membrane in preferentially transporting one ion relative to another is expressed quantitatively by the relative transport number (RTN). The RTN for a pair of ions is defined as the ratio of the fluxes of the ions through the membrane divided by the ratio of their molar concentrations in the bulk diluate. For example, the RTN for sodium ions relative to magnesium ions can be calculated as follows where molar concentrations of sodium ([Na]) and magnesium ([Mg]) ions in the ED diluate:

$$RTN_{Mg}^{Na} = \frac{\text{flux } Na}{\text{flux } Mg} \bigg/ \frac{[Na]}{[Mg]}$$

RTN<sub>Na</sub><sup>Mg</sup> is the inverse of RTN<sub>Mg</sub><sup>Na</sup>,

$$RTN_{Na}^{Mg} = 1/RTN_{Mg}^{Na}.$$

EDM consumes one equivalent of sodium chloride for each equivalent transferred from the diluate to the concentrate. Consequently, purchase of sodium chloride represents a significant portion of the operating cost, and developing the ability to recover sodium chloride from EDM concentrate and recycle it into the EDM sodium chloride stream would significantly reduce EDM operating cost.

Recovery of sodium chloride requires separation of these monovalent ions from the other ions in the concentrate. As water is recovered first through the primary RO system and second by EDM, salts which were removed from the raw water are concentrated into smaller and smaller water volumes. Consequently, EDM concentrate flows are small relative to plant capacity, but they are highly concentrated solutions. It is possible to reach such high concentrations because each EDM concentrate stream contains highly soluble salts. If the two concentrate streams are combined, however, the ions of sparingly soluble salts, such as calcium carbonate, are contained in the blended solution, and the precipitation potential of the solution increases. Therefore isolation of sodium chloride might be accomplished by first precipitating other salts with lower solubilities until ions in the solution are predominantly sodium and chloride, and then treating the EDM concentrate with electrodialysis containing monovalent membranes to concentrate sodium chloride. The sparingly soluble salts that potentially could be precipitated have commercial uses. Depending on initial water quality, these include calcium carbonate, calcium sulfate, and magnesium hydroxide.

### 1.2.3 Other Applications of Electrodialysis Technology

Electrodialysis has been used by the food and chemical industries for decades to desalinate water and to recover salts, acids, and bases from concentrated solutions. Japan has used electrodialysis with monovalent selective membranes to recover table salt from seawater since 1969 (Yamane et al. 1969; Salt Industry Center of Japan 2013). In this application, monovalent selective membranes are used to separate divalent ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ) from monovalent ions ( $\text{Na}^+$ ,  $\text{Cl}^-$ ). This serves two purposes. The content of divalent ions in the salt product is controlled and the membrane scaling potential by salts such as  $\text{CaSO}_4$  is reduced.

Electrodialysis has been used since 1985 to recover nitric acid and hydrofluoric acid from spent solutions from metal etching (Hutter-Byszewski and Bogeatzes 1988). Electrodialysis has been used to make isotonic water from natural saltwater for use as blood plasma (Quemeneur et al. 2002). The saltwater used contained the correct concentrations of divalent ions, but too much sodium. Monoselective membranes were used to remove sodium. Electrodialysis is used to produce sodium hydroxide and hydrochloric acid from sodium chloride (Mazrou et al. 1996).

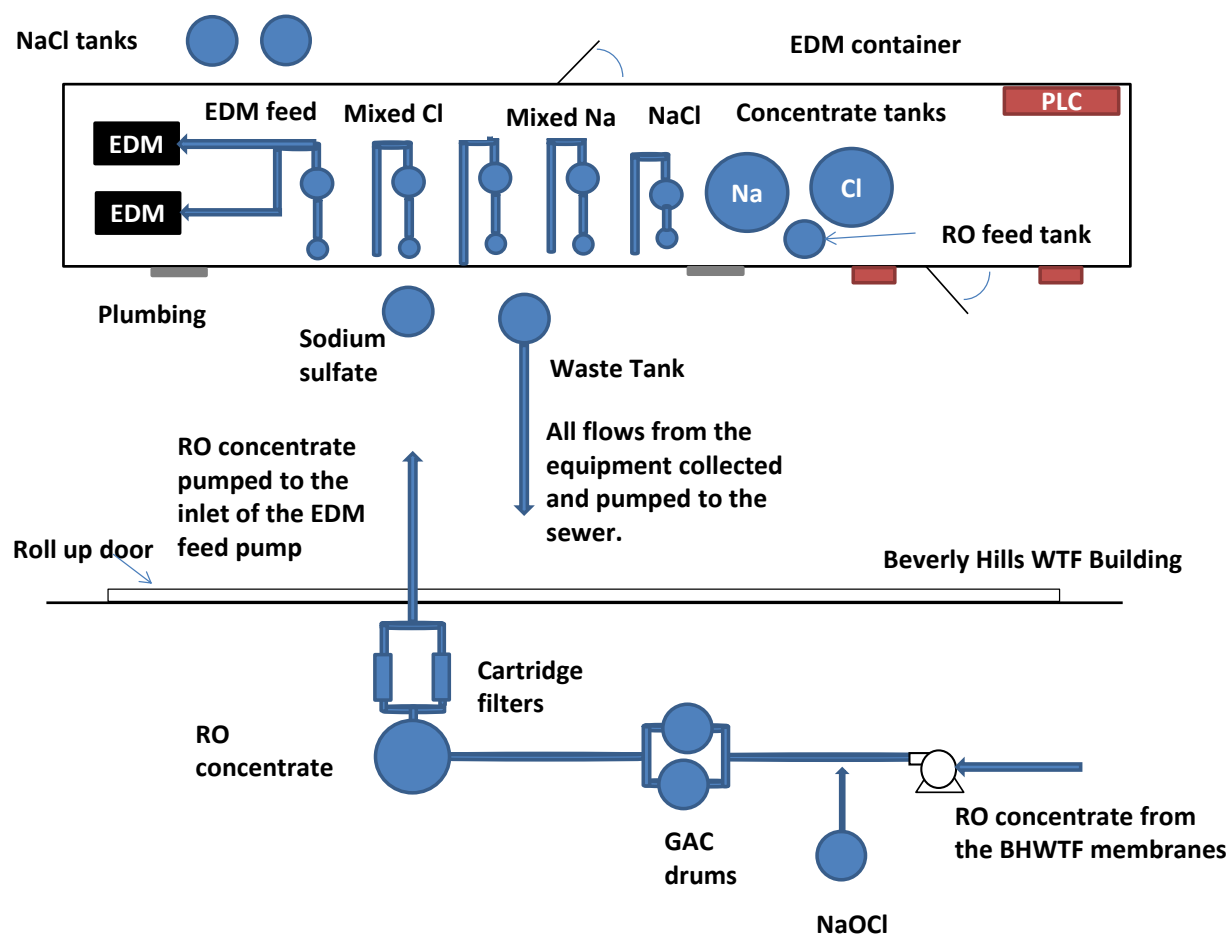
Electrodialysis is used extensively in the food industry. A few examples include the separation of whey proteins (Bazinet et al. 2004), whey lipids (Shee et al. 2005), and skim milk (Bazinet et al. 2003), and the stabilization of cloudy apple juice (Senorans et al. 2003).

## CHAPTER 2: Methods and Materials

### 2.1 Demonstration Equipment Description

Layout of the demonstration equipment at the site is represented in Figure 2.1. The EDM stacks and ancillary equipment and controls were contained in a 40 foot long shipping container. The container was set on 4 inch by 4 inch cedar timbers on the driveway at the back door of the plant building. The BHWTF brine line was tapped by Beverly Hills staff, and concentrate was pumped to the test equipment.

Figure 2.1: EDM Demonstration Equipment Layout (Plan View)



RO concentrate contained hydrogen sulfide ( $\text{H}_2\text{S}$ ) which could react with iron and manganese to form precipitates and scale the EDM membranes. Consequently pretreatment was required to remove  $\text{H}_2\text{S}$ . RO concentrate was treated with 12.5 percent strength sodium hypochlorite ( $\text{NaOCl}$ ) at a dose of 7 mg/L to oxidize hydrogen sulfide to sulfate. The only chlorine contact time occurred in the approximately 12 feet of pipe between the dosing point and the granular

activated carbon (GAC) drums. The concentrate then passed through two 55-gallon drums filled with 12 x 40 mesh bituminous GAC to remove chlorine. The GAC drums were operated in parallel, each with an empty bed contact time of approximately four minutes. GAC effluent discharged to the RO concentrate storage tank under pressure from the GAC feed pump. A sump pump in the RO concentrate storage tank pumped the concentrate through two 0.5 micrometer ( $\mu\text{m}$ ) cartridge filters in parallel to the inlet of the EDM feed pump. This flow was metered and controlled with manual valves in the EDM container.

Inside the EDM container, EDM diluate was recycled continually to the top of a 6-inch diameter standpipe connected to the inlet of the EDM feed pump. EDM feed flow was selected based on cell velocity, and flow rate of the EDM feed pump was a set point selected on the HMI (human machine interface) of the equipment control panel. Target recycle ratio was achieved by selection of the flow rate of RO concentrate into the EDM pump inlet pipe. For example, for an EDM feed flow of 25 gallons per minute (gpm) and a recycle ratio of 2.0, the RO concentrate flow was maintained at approximately 8 gpm to produce a two to one ratio of EDM diluate and RO concentrate in the EDM feed.

The mixed chloride, mixed sodium, sodium chloride, and electrode rinse streams all had a similar arrangement with a standpipe attached to a feed pump. The flow rates of these streams were automatically controlled by the programmable logic controller (PLC) to maintain equal pressures in the stack compartments. All of the standpipes had an overflow connection that discharged to waste. All flows from the test equipment were collected in a waste tank adjacent to the EDM container from which it was pumped to the sewer.

Concentrations in the sodium chloride stream were maintained by pumping sodium chloride solution from two saturation tanks outside the container into the sodium chloride standpipe. The saturation tanks were filled with high quality salt and dilution water. We used commercially available rock salt typically sold for use in home water softeners. Two brands were used during testing: Morton System Saver II Pellets and Diamond Crystal Bright Soft. Each product was reported to be up to 99.8 percent pure.

Similarly, concentrations in the electrode rinse stream were maintained by pumping sodium sulfate solution from a saturation tank outside the container into the electrode rinse standpipe. Concentrations in the mixed sodium and mixed chloride concentrate streams were maintained by periodically pumping RO permeate into the concentrate standpipes as dilution water.

Dilution water was used to flush out the EDM stack and to maintain solution concentrations. Water for flushing and dilution was supplied by an RO system inside the EDM container. BHWTF product water was pumped through a 2.5-inch diameter RO membrane. The permeate was stored in a pneumatic tank and used to dilute the concentrate streams as necessary and to flush the system after shut downs.

Photographs of the equipment at the BHWTF site are presented in Figures 2.2 through 2.7. The photographs progressively show the order of flow through the demonstration equipment, from the connection to the existing RO brine line inside the treatment plant to the EDM equipment inside the container.

The BHWTF RO skids and hoses connecting the test equipment to the RO brine line and carrying flows back to the sewer connection are shown in Figure 2.2. The green hose connected to the RO brine line of the skid shown. The blue hose carried waste flows from the pilot to a sewer connection.

The concentrate pump, chlorine feed, and GAC drums are shown in Figure 2.3. Concentrate was dosed with chlorine upstream of the GAC to oxidize hydrogen sulfide. The chlorine residual was removed in the GAC.

In Figure 2.4, the GAC drums were connected to the concentrate storage tank. Concentrate was pumped from this tank to the EDM feed pump inlet pipe.

The EDM container and waste storage tank are shown in Figure 2.5. The container sits a few feet outside the open doorway in Figure 2.4. Figures 2.6 and 2.7 show the inside of the EDM container.

**Figure 2.2: Beverly Hills RO membrane skids.**



The green hose carried concentrate from the RO brine line to the test equipment. The blue hose carried all flows from the waste storage tank to the sewer connection.

**Figure 2.3: Hydrogen sulfide removal.**



Flow from the BHWTF brine line was dosed with chlorine and pumped through two 55-gallon drums of GAC operated in parallel.

**Figure 2.4: EDM feed tank.**



After the GAC, RO concentrate was stored in the tank shown and pumped to the suction pipe of the EDM feed pump.

**Figure 2.5: Exterior of EDM equipment container.**



EDM equipment was contained in a 40-foot-long shipping container. Flows from the container were collected in a waste storage tank outside the container and pumped to the sewer connection inside the building

**Figure 2.6: Interior of the EDM equipment container.**



Standpipes and pumps for the five EDM streams are aligned along the wall on the left side of the photograph. The EDM stack is at the end of the container (far wall in the photograph).



**Figure 2.7: EDM standpipes.**



Each EDM stream had a standpipe connected to the influent line of its pump. Overflow lines at the top of each standpipe discharge to the waste storage tank.

## **2.2 Testing Description**

The following nine experiments were conducted during testing:

- Experiment 1 – evaluation of hydrogen sulfide removal with chlorine followed by GAC for dechlorination.
- Experiment 2 – evaluation of EDM set points and limiting current density.
- Experiment 3 – evaluation of EDM stack resistance.
- Experiment 4 – evaluation of EDM concentrate streams.
- Experiment 5 – evaluation of EDM relative transport numbers.
- Experiment 6 – evaluation of water transported through the EDM membranes.
- Experiment 7 – evaluation of EDM recovery.
- Experiment 8 – treatment of EDM concentrate streams by precipitation.
- Experiment 9 - treatment of EDM concentrate streams with electrodialysis.

### **2.2.1 Experiment 1: Evaluation of pretreatment to remove hydrogen sulfide**

A bench-scale experiment was conducted to evaluate the success of pretreatment to remove hydrogen sulfide in the RO concentrate with chlorine followed by contact with GAC to dechlorinate the concentrate. The objectives were to determine the chlorine dose required to

oxidize hydrogen sulfide in the RO concentrate and then to ensure residual chlorine would be removed by GAC. Experiment 1 was not directly germane to the research objectives of this project, but pretreatment removal of hydrogen sulfide was necessary to avoid fouling the EDM membranes with sulfide precipitates. Experiment 1 was conducted to ensure adequate removal of hydrogen sulfide ahead of the EDM membranes.

A sample of RO concentrate was collected from BHWTF's concentrate sample tap. Chlorine doses ranging from 1 mg/L to 29 mg/L were added to the sample in five jars. Chlorine residual and pH were measured in the chlorinated samples. The samples were then slowly poured through a 1-inch diameter PVC column containing a 6-inch depth of 12x40 mesh bituminous GAC. Chlorine residual and pH were measured in the GAC effluent and samples were poured for laboratory analysis of hydrogen sulfide.

### 2.2.2 Experiment 2: Evaluation of EDM limiting current density and limiting polarization parameter

The objective of Experiment 2 was to determine limiting current density and the limiting polarization parameter for the EDM stack. Cell velocity and recycle ratio were selected for each condition tested. The stack was opened prior to Experiment 2, and we determined the stack contained 90 quads. The EDM feed flow rate was calculated using cell velocity for a 90-quad stack. Flow rate from the RO concentrate storage tank was metered. This flow was controlled manually by valve adjustment to achieve the RO concentrate flow required to meet the target recycle ratio.

EDM stack voltage was increased incrementally. When current stabilized at each voltage step, we measured EDM feed and diluate conductivities and recorded the voltage and current. We entered these values concurrently into a spreadsheet to develop a graph of the relationship between voltage and current density. The experiment was stopped when the current-voltage curve appeared to be flat.

The limiting current density was calculated according to the following semi-empirical formula based on Bard and Faulkner's (1980) Eq. 1.4.25 for limiting current density:

$$i = i_{lim} \left\{ 1 - \exp \left[ \frac{U_{applied} - U_{cell}}{C} \right] \right\}$$

where  $i$  is the current density;  $i_{lim}$  is the limiting current density;  $U_{applied}$  is the applied voltage difference across the stack electrodes;  $U_{cell}$  is the open cell voltage of the stack; and  $C$  is a model fitting constant. Non-linear regression with least-squares and 1/X weighting was used to determine the best-fit values of the three parameters ( $i_{lim}$ ,  $U_{cell}$ , and  $C$ ), simultaneously.

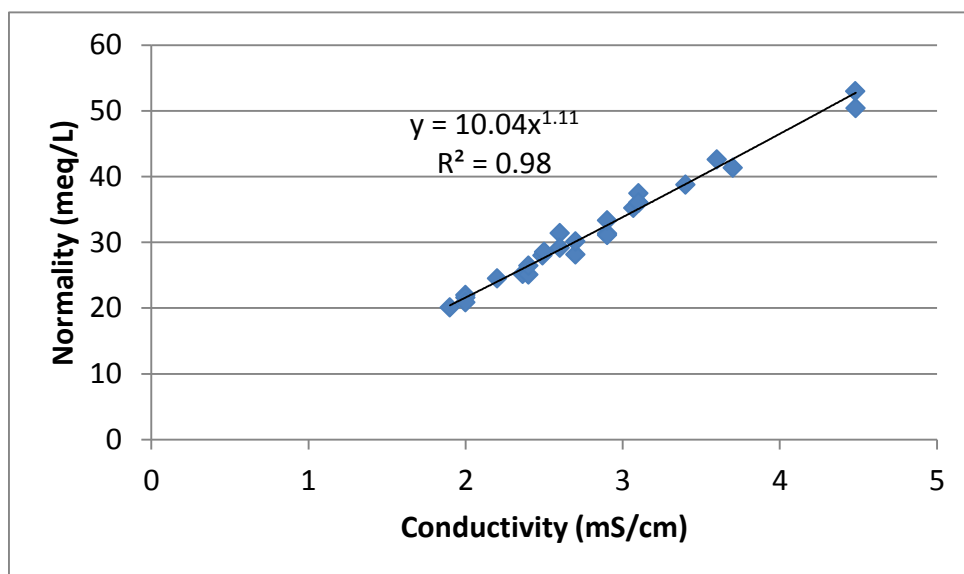
Normalities of the feed and diluate streams were estimated using the relationship shown in Figure 2.8. The data in this graph are conductivities and normalities in the EDM feed and diluate from water quality samples collected during operation.

Polarization parameter was calculated as follows where  $i$  is current density and  $Nm$  is the log mean of the EDM influent normality ( $Ni$ ) and diluate normality ( $Nd$ ).

$$PP = \frac{i}{Nm}$$

$$Nm = \frac{(Ni - Nd)}{\ln\left(\frac{Ni}{Nd}\right)}$$

**Figure 2.8: Correlation between conductivity and normality in the EDM feed and diluate**



### 2.2.3 Experiment 3: Evaluation of EDM stack resistance

The objective of this experiment was to measure resistance in the EDM stack and to monitor stack resistance throughout testing. Resistance is the reciprocal of conductance; therefore as conductivity decreases, resistance increases. The resistance measured in this experiment is affected by conductivity in each of the EDM streams, and therefore resistance is expected to vary slightly at different points during testing. Nevertheless, a significant increase in stack resistance at any time during the test period could indicate membrane fouling. This experiment was conducted throughout the test period to monitor any changes in EDM performance.

EDM feed flow and recycle ratio were set as described for Experiment 1. Voltage was increased incrementally and current readings were recorded when the system reached steady-state. Voltage was plotted against current to evaluate stack resistance.

### 2.2.4 Experiment 4: Evaluation of EDM concentrate streams

The objective of Experiment 4 was to determine the effectiveness of EDM in separating ions into two concentrate streams of high solubility. If the membranes were 100 percent selective, only anions would be transported from the EDM feed to the mixed sodium stream and only cations

would be transported from the EDM feed to the mixed chloride stream. The membranes, however, allow some passage of cations to the mixed sodium stream and some anions to the mixed chloride stream. Furthermore, impurities in the NaCl stream--ions other than sodium or chloride--may be transferred from the sodium chloride compartments to the concentrate compartments.

Samples of the EDM feed, diluate, sodium chloride, and concentrate streams were collected periodically during testing for laboratory analyses. The laboratory results were evaluated to determine the extent to which EDM prevented cation transport to the mixed chloride stream and anion transport to the mixed sodium stream. All laboratory analyses were conducted by Eaton Analytical.

### 2.2.5 Experiment 5: Evaluation of EDM relative transport numbers

The objective of Experiment 5 was to determine the relative number of ions transported across the four membranes during operation. The experiment was conducted periodically during testing under a variety of operating conditions.

The research team collected samples from the EDM feed, EDM diluate, mixed sodium concentrate, mixed chloride concentrate, and sodium chloride streams for laboratory analyses. The research team used the laboratory results to calculate relative transport numbers.

For example, the RTN for the ratio of sodium to magnesium transported from the diluate to the mixed chloride concentrate is defined as the ratio of the flux of each ion from the diluate into the concentrate divided by the molar ratio of the two ions in the diluate.

$$RTN_{Mg}^{Na} = \frac{flux\ Na}{flux\ Mg} \bigg/ \frac{[Na]_d}{[Mg]_d}$$

$$\frac{flux\ Na}{flux\ Mg} = \frac{[Na]_f - [Na]_d}{[Mg]_f - [Mg]_d}$$

The flux ratio was calculated as difference between the feed and diluate molar concentrations of sodium divided by the same difference for magnesium. This ratio was divided by the ratio of molar concentrations of sodium to magnesium in the diluate.

### 2.2.6 Experiment 6: Evaluation of water transported through the EDM membranes

The objective of Experiment 6 was to determine the amount of water transported with ions through the membranes. The water carried through the membranes with ions by osmosis and electroosmosis from the feed compartment to the concentrate compartments is lost as product water. Understanding the rate of water transferred through the membranes allows us to better predict recoveries possible in EDM systems.

During Experiment 6, the research team collected each concentrate stream over a set time and recorded the volume collected. Concentrate flow rates ( $q_c$ ) were calculated as the volume ( $V_c$ ) collected divided by the collection period ( $t_c$ ).

$$q_c = \frac{V_c}{t_c}$$

During normal operation some deionized water was added to the concentrate streams to maintain the solution below solubility limits. Dilution frequency and duration were operator set points. For example, dilution might be set to occur for a period of 2 minutes once every 12 minutes.

The research team set the dilution rate to zero for each concentrate stream during Experiment 6 to ensure only water transported across the membranes was measured. The measurement was repeated at least four times for each condition, and the concentrate flow rate was calculated using the average of these measurements.

While concentrations in the mixed sodium and mixed chloride concentrate streams are largely a byproduct of influent water quality and treatment goals, concentration in the sodium chloride stream is an operating parameter that is set and controlled by the operator. Furthermore, EDM can be operated over a range of concentrations in the sodium chloride stream. We repeated the experiment across a range of concentrations in the sodium chloride stream to evaluate the effect of sodium chloride concentration on transport of water across the membranes.

Cell velocity was held constant throughout the experiment. We tested a total of six conditions: three sodium chloride concentrations, each at two different EDM stack currents. At the end of the experiment, samples of the EDM feed, EDM diluate, two concentrates, and sodium chloride streams were collected for laboratory analyses. The experiment results were used to calculate the water transported across the membranes with ions as follows, where  $\lambda$  (mole/eq) is the water transport rate,  $q_c$  (L/min) is the concentrate flow rate,  $q_f$  (L/min) is the EDM feed flow rate, and  $\Delta N$  (eq/L) is the difference in normality between the EDM feed and diluate.

$$\gamma = \frac{q_c}{\Delta N q_f} \times 0.018 \frac{\text{mole}}{L}$$

### 2.2.7 Experiment 7: Evaluation of EDM recovery

The mass balance diagram in Figure 2.9 shows the flows used to calculate recovery for EDM and for the system as a whole. The dashed line represents the control volume for water mass balance equations used to calculate water recovery. The flows entering the volume are the RO concentrate, dilution water to each of the EDM concentrate streams, and the sodium chloride makeup solution. The flows leaving the system are EDM diluate, mixed sodium concentrate, and mixed chloride concentrate. EDM recovery was defined as the ratio of EDM diluate to RO concentrate.

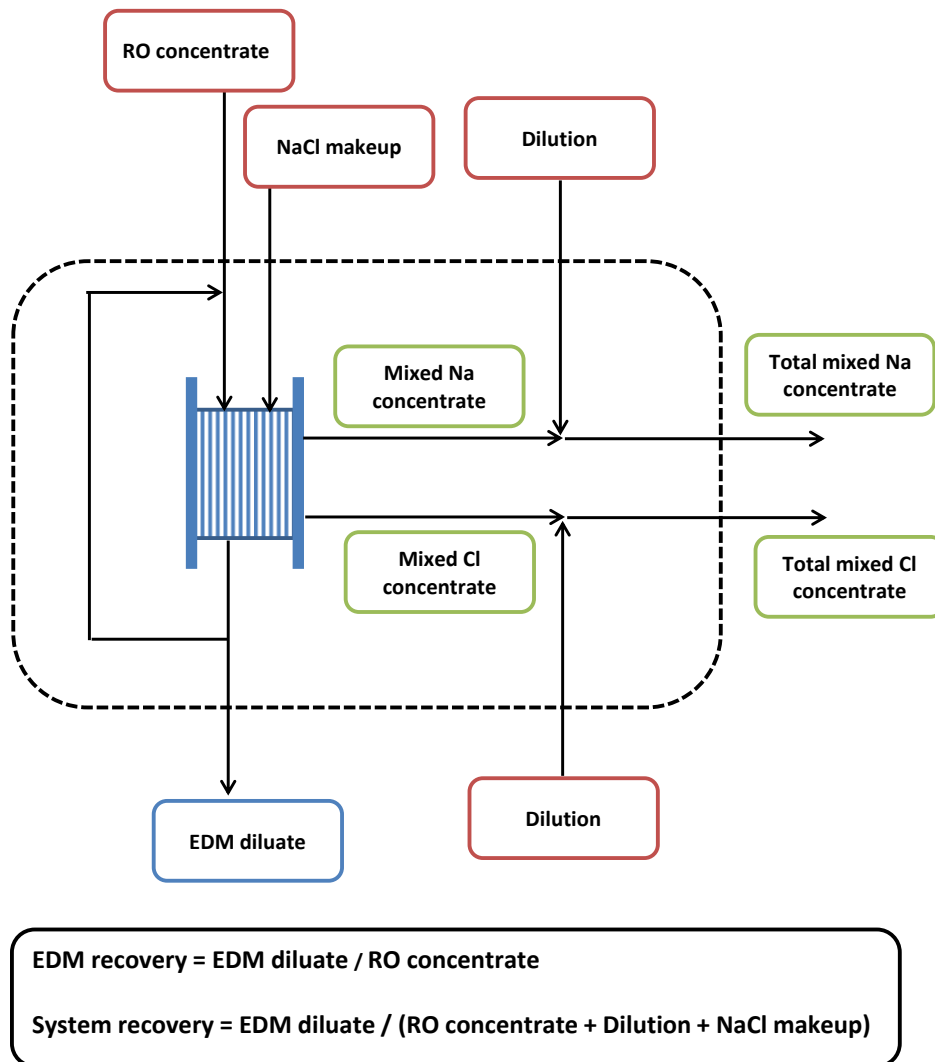
$$\text{EDM stack recovery} = \frac{\text{EDM diluate}}{\text{RO concentrate}}$$

For the overall system recovery, dilution and NaCl makeup water flows into the control volume were also considered. System recovery was calculated as follows.

$$EDM \text{ system recovery} = \frac{EDM \text{ diluate}}{RO \text{ concentrate} + Dilution + NaCl \text{ makeup}}$$

DI dilution water was measured with the DI water flow totalizer. Water transported through the membranes into the concentrate compartments was measured volumetrically as described for Experiment 6. Feed flow was measured with a magnetic meter and with a rotameter.

**Figure 2.9: Water mass balance diagram for calculation of EDM recovery.**



### 2.2.8 Experiment 8: Evaluation of treatment of the two EDM concentrate streams by precipitation

The objective of Experiment 8 was to evaluate treatment of EDM concentrate by precipitation, with and without chemical addition to adjust pH. The mixed sodium stream was rich in sulfate and carbonate. The mixed chloride stream was rich in calcium and magnesium. When the concentrate streams are mixed, the blended solution may be supersaturated with respect to one or more sparingly soluble salts. Consequently, there is potential to remove divalent ions from

the combined EDM concentrate by precipitation of salts such as calcium sulfate ( $\text{CaSO}_4$ ), calcium carbonate ( $\text{CaCO}_3$ ), and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ).

The research team conducted this EDM concentrate treatment experiment at bench-scale and at pilot-scale. In the bench-scale tests, we mixed 400-mL volumes of blended concentrate on a plate stirrer with and without chemical addition to increase pH. The chemicals used to increase pH were caustic ( $\text{NaOH}$ ), soda ash ( $\text{Na}_2\text{CO}_3$ ), or both. The samples were filtered through a 1  $\mu\text{m}$  filter into bottles for laboratory analysis.

In the pilot-scale version of this experiment, the research team discharged each concentrate stream into a 50-gallon tank. When sufficient volumes were collected, we combined the two concentrate volumes into one tank. Hence, the streams were blended in proportion to their production during treatment. The blended concentrate volume was mixed with a  $\frac{1}{4}$  horsepower mixer for two hours. We collected samples for water quality analyses at 5 minutes, 30 minutes, 60 minute, and 120 minutes. The samples were filtered through a 1  $\mu\text{m}$  bag filter into bottles for shipment to the laboratory. As with the bench-scale test, this test was conducted with and without chemical addition, but only  $\text{NaOH}$  was used since bench-scale results showed  $\text{Na}_2\text{CO}_3$  was not needed.

#### 2.2.9 Experiment 9: Evaluation of treatment of the two EDM concentrate streams by electrodialysis

Each of the EDM concentrate streams has high concentrations of sodium chloride because they contain the sodium and chloride removed from the EDM feed plus the sodium and chloride transferred from the sodium chloride stream. The ability to recover sodium chloride from the EDM concentrate and reuse it in the EDM sodium chloride stream would reduce EDM operating costs significantly.

The objective of Experiment 9 was to evaluate treatment to recover sodium chloride from the EDM concentrate streams by first treating the concentrate in a precipitation step (evaluated in Experiment 8) followed by electrodialysis (ED) with monovalent ion selective membranes.

The mixing basin is shown in Figure 2.9. The research team collected the two EDM concentrate streams in a 50-gallon tank during normal operation. We dosed the blended concentrate with 6,000 mg/L of  $\text{NaOH}$ , mixed the sample for 5 minutes, and allowed the volume to settle. We collected clarified water from the tank and treated it in an electrodialysis stack containing monovalent ion-selective membranes. The goal was to produce a sodium chloride-rich stream in the ED concentrate through transfer of mostly sodium and chloride (the predominant monovalent ions present) from the ED diluate to the ED concentrate.

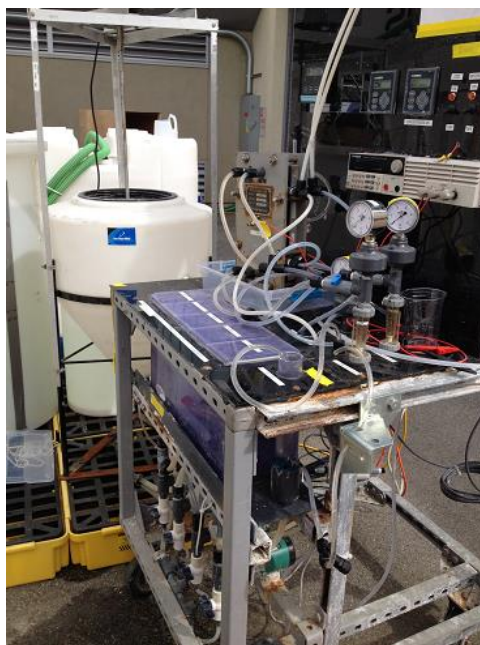
The research team measured electrical conductivity in the diluate and concentrate streams throughout the experiment. The experiment was concluded when conductivity in the concentrate stream reached 196 mS/cm. Sodium chloride reaches saturation at around 200 mS/cm. Samples of the ED feed and concentrate were collected for laboratory analyses.

**Figure 2.8: ED feed tank.**



Supernatant from the precipitation step was collected in the ED feed tank shown below. Diluate was recirculated through the feed tank until conductivity in the concentrate reached 192 mS/cm.

**Figure 2.9: Electrodialysis stack**



A small electrodialysis stack containing monovalent ion-selective membranes was used to concentrate sodium chloride.



## 2.3 Concentrate Water Quality Evaluated

The research team evaluated treatment of RO concentrate with EDM at three sites in California: the Beverly Hills Water Treatment Facility, the Arcadia Water Treatment Plant in Santa Monica, and the Santa Rosa Water Reclamation Facility (SRWRF) operated by the Rancho County Water District (RCWD). We conducted the full-scale stack demonstration with the BHWTF RO concentrate. We performed desktop evaluations on the other two RO concentrates.

Average concentrate water quality for the three sites evaluated are shown in Table 2.1. Water quality data for Beverly Hills and Santa Monica were from laboratory analyses of concentrate samples collected at the Beverly Hills Water Treatment Facility and the Arcadia Water Treatment Plant. The Santa Rosa Water Reclamation Facility (SRWRF) evaluation via modeling assumes treatment of RO brine for reuse, since implementation of RO is in the planning stage. Water quality of the tertiary treated wastewater effluent with the RO membrane design software (Hydranautics Membrane Solutions Design Software, v. 2012) was used to project RO concentrate concentrations at SRWRF. The evaluation was conducted with RO membranes predicted to achieve 96 percent rejection of TDS and at an RO recovery of 85 percent.

**Table 2.1: Average concentrate water quality for the sites evaluated**

		<b>Beverly Hills</b>	<b>Rancho Water</b>	<b>Santa Monica</b>
Calcium	mg/L	157	350	635
Magnesium	mg/L	119	119	255
Sodium	mg/L	537	919	447
Potassium	mg/L	16	89	17
Sulfate	mg/L	470	839	1365
Chloride	mg/L	511	1208	566
Bicarbonate	mg/L	791	938	1972
Nitrate	mg/L	0.4	203	---
Silica	mg/L	118	118	172
pH	SU	7.6	7.8	7.8
TDS	mg/L	3190	4791	4333
Conductivity	mS/cm	4.126	5.99	5.53

## 2.4 Properties of the EDM Stack Tested

Properties of the EDM stack tested at the BHWTF are shown in Table 2.2. The spacer width between membranes was 0.08 centimeters (cm). The membranes had an effective area of 4,083 square centimeters (cm<sup>2</sup>). Quad is the term used for the repeating unit of four membranes and four compartments in the EDM stack. The EDM stack tested contained 90 quads. The cation

exchange membranes were model RALEX CM(H)-PES by Mega, and the anion exchange membranes were model RALEX AM(H)-PES by Mega. The membranes are heterogeneous ion exchange membranes composed of fine polymer particles with ion exchange groups anchored by a polymer matrix. Area resistances were 7.5 ohms per square centimeter ( $\Omega/\text{cm}^2$ ) for the cation exchange membranes and 8.0  $\Omega\text{ cm}^2$  for the anion exchange membranes. The anode was titanium/plutonium (Ti/Pt), and the cathode was stainless steel. Sodium sulfate was used for the electrolyte solution.

**Table 2.2: Properties of EDM stack tested**

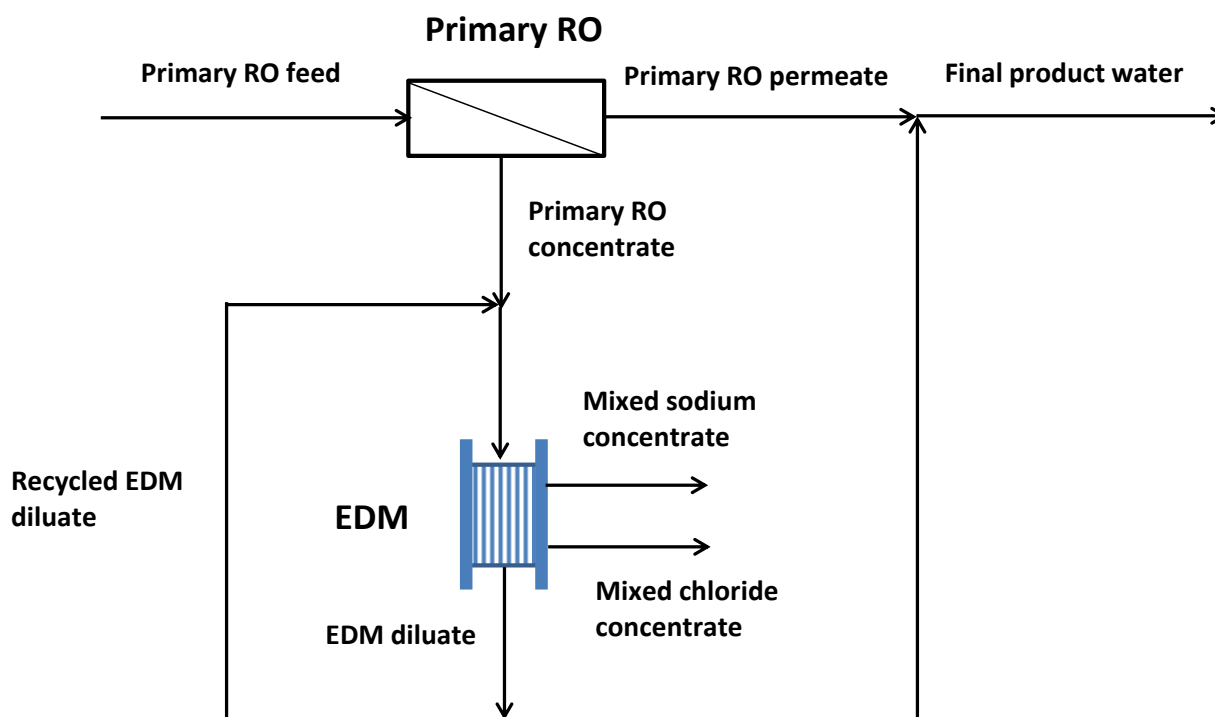
EDM membrane spacer width (cm)	0.08
EDM membrane width (cm)	40
EDM membrane length (cm)	160
EDM membrane effective area ( $\text{cm}^2$ )	4083
EDM number of quads	90
Cation Exchange membrane	RALEX CM(H)-PES
Anion Exchange membrane	RALEX AM(H)-PES
EDM cation exchange membrane area resistance ( $\Omega\text{ cm}^2$ )	7.5
EDM anion exchange membrane area resistance ( $\Omega\text{ cm}^2$ )	8.0
Anode	Ti/Pt
Cathode	Stainless steel

## CHAPTER 3: Results and Discussion

### 3.1 Treatment Approach Evaluated during Testing

The treatment approach evaluated during testing is shown in Figure 3.1. Concentrate from the existing RO membranes was treated in EDM. EDM produced a diluate (product) stream and two concentrate streams, one containing mostly cations mixed with chloride, referred to as the mixed chloride concentrate, and the other containing predominantly anions with sodium referred to as the mixed sodium concentrate. A portion of the diluate was recycled and blended with the RO concentrate to create the EDM feed. In a full-scale application, EDM diluate would be blended with RO permeate to produce the final product water.

**Figure 3.1: RO concentrate treatment approach evaluated during testing**



Throughout this study, recycle ratio was defined as the ratio of recycled EDM diluate to RO concentrate in the EDM feed flow. For example, a recycle ratio of 2 meant the EDM feed comprised two parts recycled EDM diluate and one part primary RO concentrate. Recycling diluate reduces TDS in the EDM influent and therefore reduces the number of ions that must be removed by EDM to meet a specific treatment goal. The disadvantage of recycling the EDM diluate is that it increases the EDM throughput capacity required.

## 3.2 Test Results

As discussed in Chapter 2, the following nine experiments were conducted during testing:

- Experiment 1 – evaluation of hydrogen sulfide removal with chlorine followed by GAC for dechlorination.
- Experiment 2 – evaluation of EDM set points and limiting current density.
- Experiment 3 – evaluation of EDM stack resistance.
- Experiment 4 – evaluation of EDM concentrate streams.
- Experiment 5 – evaluation of EDM relative transport numbers.
- Experiment 6 – evaluation of water transported through the EDM membranes.
- Experiment 7 – evaluation of EDM recovery.
- Experiment 8 – treatment of EDM concentrate streams by precipitation.
- Experiment 9 - treatment of EDM concentrate streams with electrodialysis.

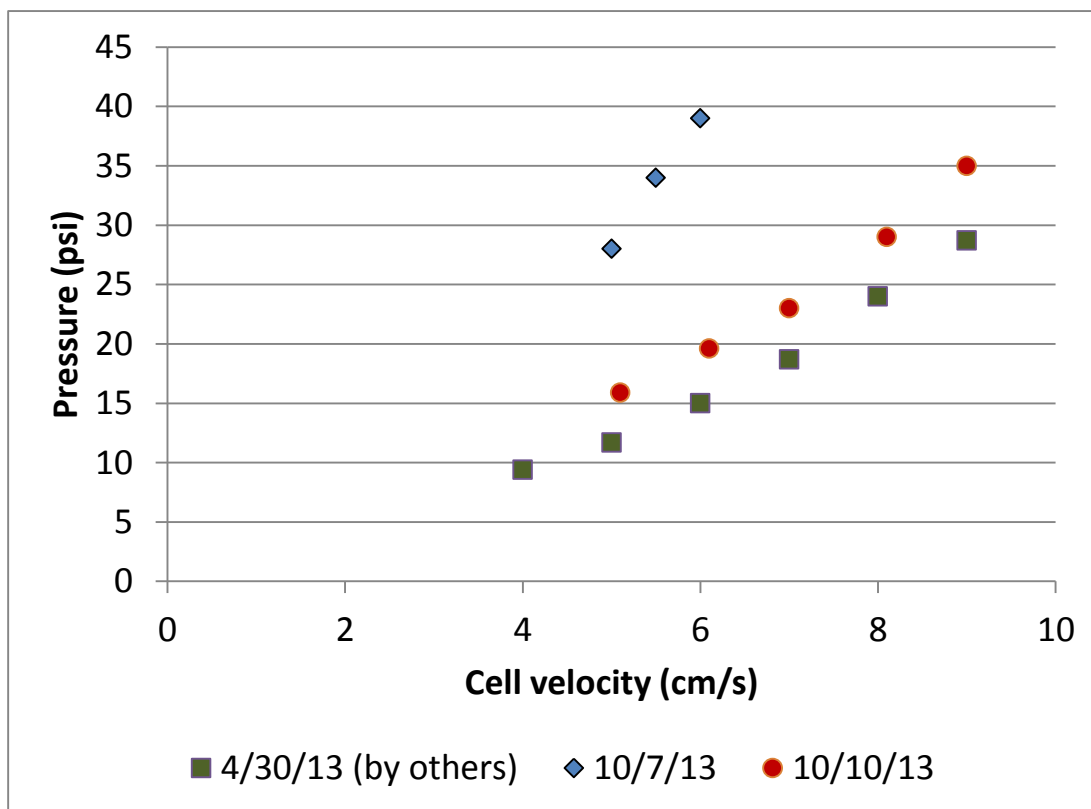
Prior to start up, Veolia, the equipment provider, performed a clean-in-place (CIP) on the stack using the following protocol:

- Replace fluid in all streams except the electrode rinse stream with RO permeate.
- Circulate the RO permeate at 15 to 20 gpm in each stream.
- Add NaCl solution to the standpipe using chemical feed pump until conductivity is between 50 and 100 mS/cm.
- Fill a 5-gallon bucket with RO permeate about 2/3 full and pour NaOH and stir until pellets are dissolved.
- Add NaOH solution to the standpipes until pH is between 12 and 13.
- Circulate for 30 to 60 minutes.
- Soak overnight.
- Drain and replace the solutions with RO permeate.

The research team recorded EDM feed pressures across a range of cell velocities to evaluate the effectiveness of the clean-in-place (CIP) procedure (Figure 3.2). Three sets of data are shown. The data from April, 30, 2014 are from testing with this stack and membranes at another site and for another project when the membranes were new. These data are included to provide a benchmark for expected pressure results. The pressure data collected October 7, 2013 after the second CIP at the site were more than twice the pressures measured on April 30, 2013. Consequently, the CIP procedure was repeated, but there was no reduction in pressure after the second CIP. When the second CIP failed to improve pressures in the system, the EDM stack was

taken apart. During this procedure, the membranes were inspected and wiped off and some were replaced. The stack was reassembled. After dismantling the stack and reassembling it, pressures were measured October 10, 2013 and found to be much closer to the pressures measured on April 30, 2013. Furthermore, the pressure curves are parallel, indicating the rate of pressure loss with velocity was the same as it was before delivery to the site. The research team concluded the stack was ready for testing. The reassembled stack contained 90 quads.

**Figure 3.2: EDM stack pressures prior to delivery to the site (4/30/13), after two CIPs at the site (10/7/13), and after taking the stack apart and reassembly (10/10/13)**



### 3.2.1 Experiment 1: Evaluation of pretreatment to remove hydrogen sulfide

A bench-scale experiment was conducted to evaluate pretreatment to remove hydrogen sulfide in the RO concentrate with chlorine followed by treatment with GAC to dechlorinate the concentrate. The objectives were: 1) to determine the chlorine dose required to oxidize hydrogen sulfide from the RO concentrate and 2) to ensure residual chlorine would be removed by the GAC.

The results of this test are shown in Table 3.1. Chlorine doses ranged from approximately 1 mg/L to 29 mg/L. The hydrogen sulfide level in the concentrate tested was 0.4 mg/L. Hydrogen sulfide was reduced to below detection levels at all chlorine doses tested. The GAC was effective for removing the chlorine residual in all samples except for the sample dosed with 29 mg/L. A chlorine residual of 0.8 mg/L was measured in that sample.

The research team made the following decisions based on these test results:

- Testing would start with a 2 mg/L chlorine dose.
- Hydrogen sulfide in the GAC effluent would be measured daily. If hydrogen sulfide was detected, the chlorine dose would be increased until H<sub>2</sub>S was no longer present.
- Chlorine residual in the GAC effluent would be measured daily.
- A HACH field kit for measuring hydrogen sulfide was purchased and used to monitor H<sub>2</sub>S in the GAC effluent.

**Table 3.1: Experiment 1 results showing chlorine and hydrogen sulfide residuals after treatment**

Jar	Chlorine dose (mg/L)	After chlorination		After GAC		
		pH (SU)	Cl <sub>2</sub> (mg/L)	pH (SU)	Cl <sub>2</sub> (mg/L)	H <sub>2</sub> S (mg/L)
1	0.9	7.3	0.2	7.8	0.1	BDL
2	1.8	7.2	0.3	8.0	0.1	BDL
3	4.8	7.4	0.1	8.1	0.1	BDL
4	9.7	7.3	0.2	7.9	0.1	BDL
5	28.9	7.2	1.9	7.9	0.8	BDL
BDL = below method detection limit						

### 3.2.2 Experiment 2: Evaluation of EDM limiting current density

The objective of Experiment 2 was to evaluate limiting current density for the EDM stack. Four cell velocities were tested with a recycle ratio of 1.5. Voltage was increased, and EDM feed and diluate conductivities were measured. Measurements were stopped when it appeared the limiting current density was reached. The polarization parameter was calculated for each condition at the limiting current density as follows where  $N_i$  is the EDM feed normality,  $N_d$  is the EDM diluate normality, and  $N_m$  is the log mean of the EDM feed and diluate normalities:

$$PP = \frac{i}{N_m}$$

$$N_m = \frac{(N_i - N_d)}{\ln\left(\frac{N_i}{N_d}\right)}$$

The results of Experiment 2 are shown in Figures 3.3 through 3.6. The limiting current density was calculated for each cell velocity using the formula described in section 2.2.2. The square of the correlation coefficient ( $r^2$ ) was greater than 0.99 for each graph, showing that the formula fit the data very well.

Figure 3.3: Condition 1 – Current density vs. voltage for a cell velocity of 4.0 cm/s.

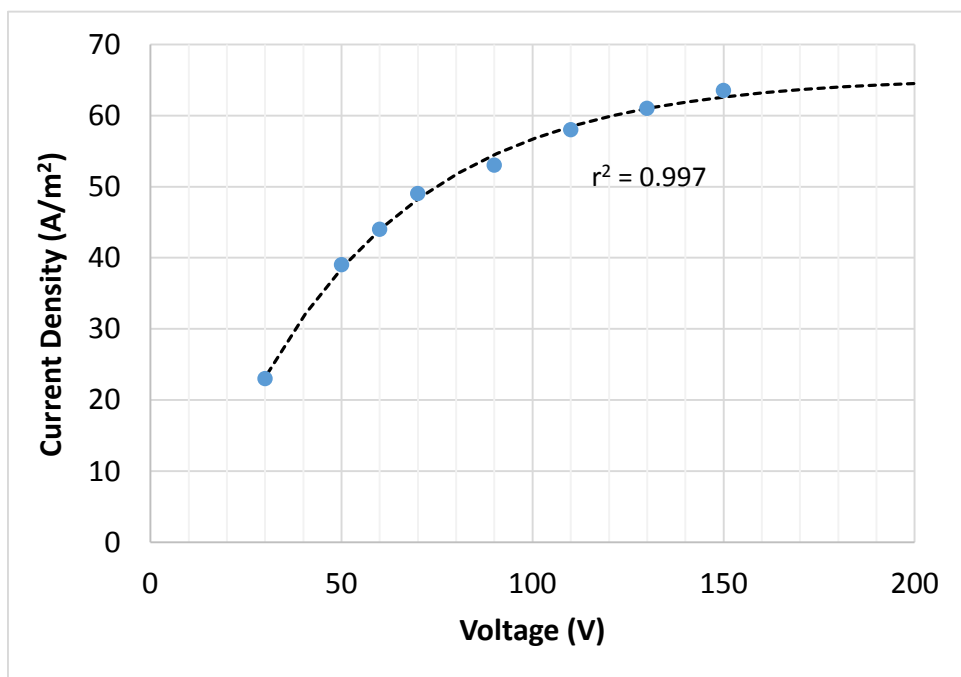


Figure 3.4: Condition 2 – Current density vs. voltage for a cell velocity of 5.0 cm/s.

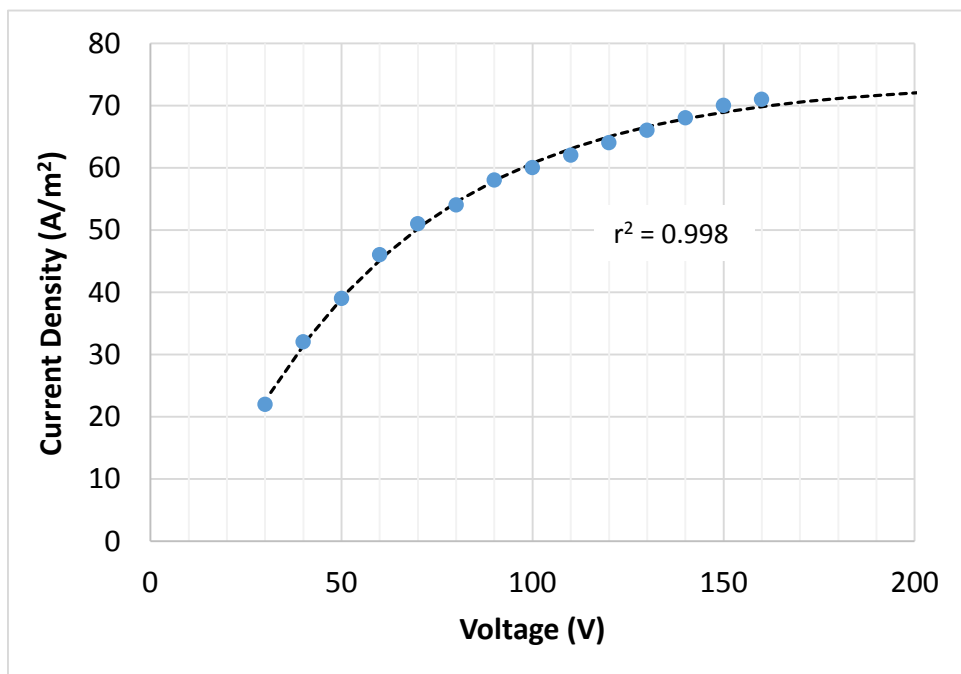


Figure 3.5: Condition 3 – Current density vs. voltage for a cell velocity of 6.0 cm/s.

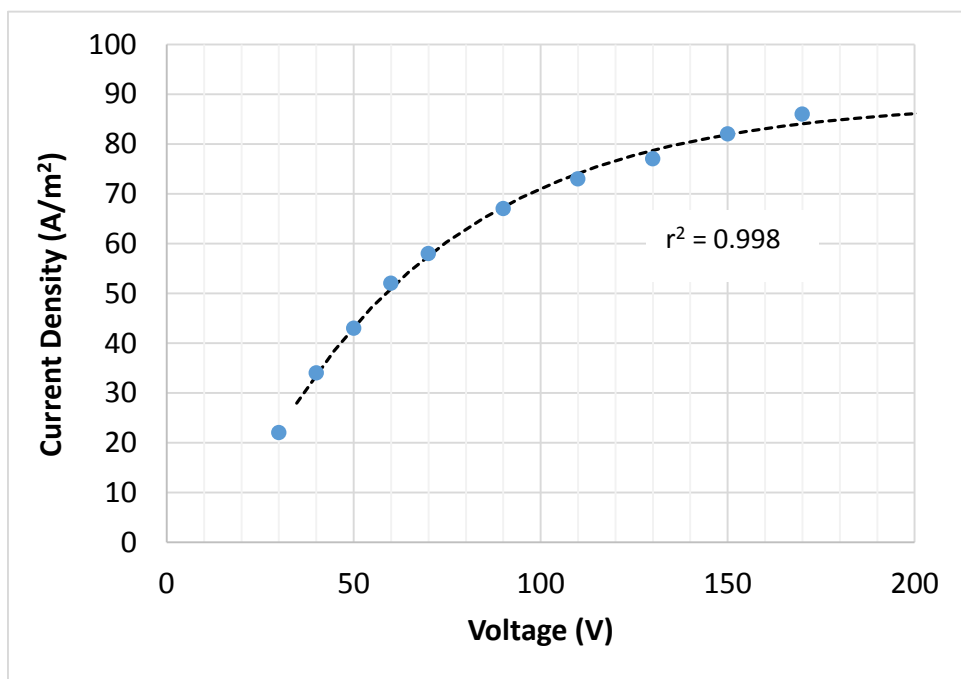
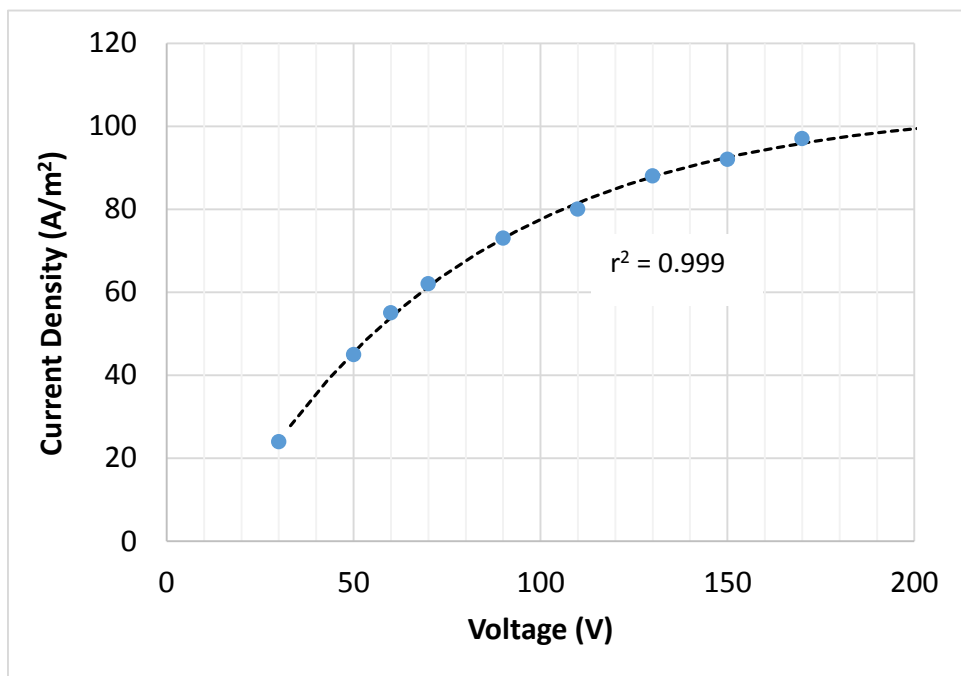


Figure 3.6: Condition 4 – Current density vs. voltage for a cell velocity of 7.0 cm/s.





The test results are summarized in Table 3.2. Limiting current density and limiting polarization parameter increased with cell velocity as expected.

**Table 3.2: Experiment 2 results**

Condition	Water temp (°F)	Cell velocity (cm/s)	Limiting current density (A/m <sup>2</sup> )	Limiting PP (A-cm/eq)
1	77	4.0	65.4	421
2	77	5.0	73.9	516
3	77	6.0	88.8	528
4	77	7.0	105.4	580

As discussed in Section 1.2.2, Davis and Lacey (1970) reported the limiting polarization parameter to be a function of cell velocity to the 0.6 power.

$$PP_{lim} = k v^{0.60}$$

Limiting polarization parameter was plotted against cell velocity in Figure 3.7 and found a similar relationship with the data fitting velocity to the 0.54 power and a “k” factor of 206.

$$PP_{lim} = 206 v^{0.54}$$

The spacer used in this EDM stack was the same Vexar spacer tested previously by Davis and Lacey (1970). Davis and Lacey reported a “k” factor of 216 with an exponent of 0.6. Consequently, the result in this test agreed with their findings.

### 3.2.3 Experiment 3: Evaluation of EDM stack resistance

Resistance was measured periodically during testing to monitor for any changes in EDM performance. For example, short circuiting of the stack or membrane scaling could be indicated by an increase in stack resistance.

Voltage and current measurements recorded periodically from November 2013 through March 2014 are shown in Figure 3.8. The slope of the graph is the resistance in ohms. EDM stack performance was consistent across these measurements.

Figure 3.7: Experiment 2 relationship between limiting polarization parameter and cell velocity.

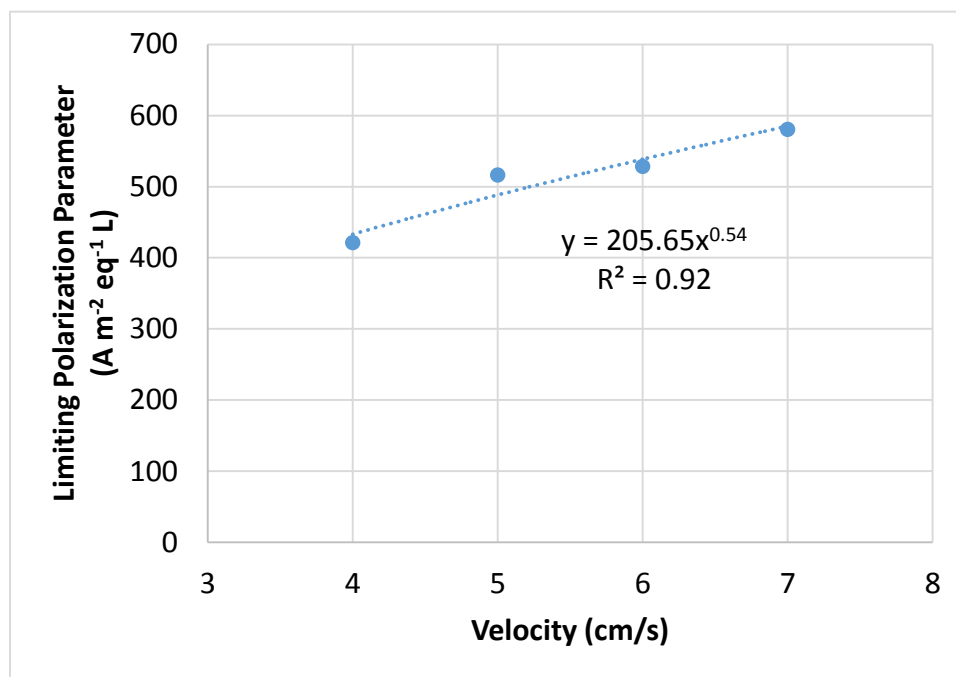
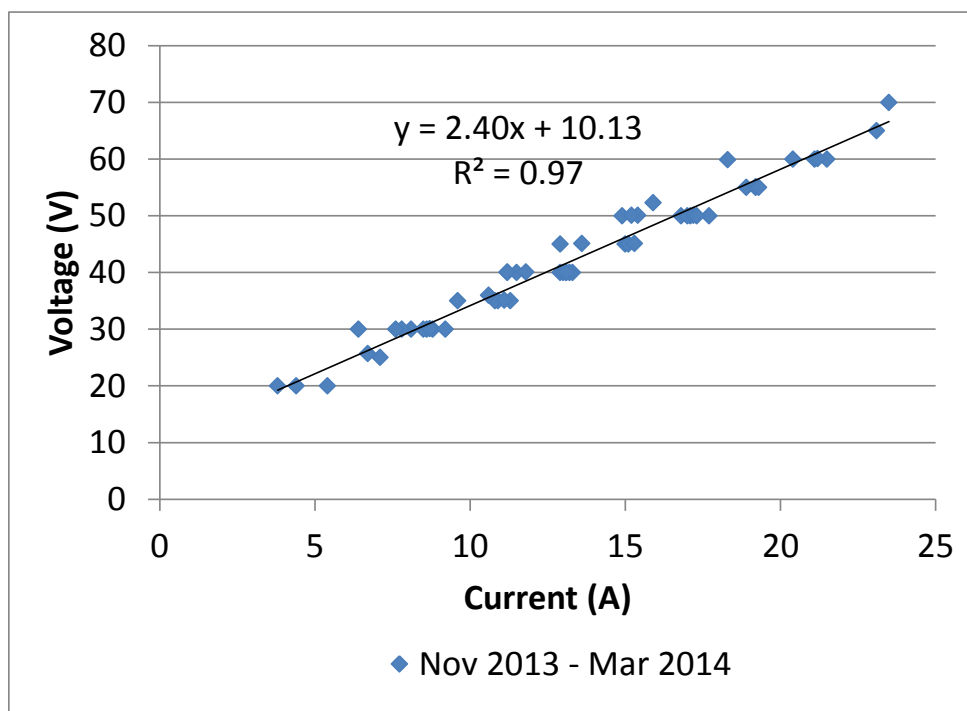
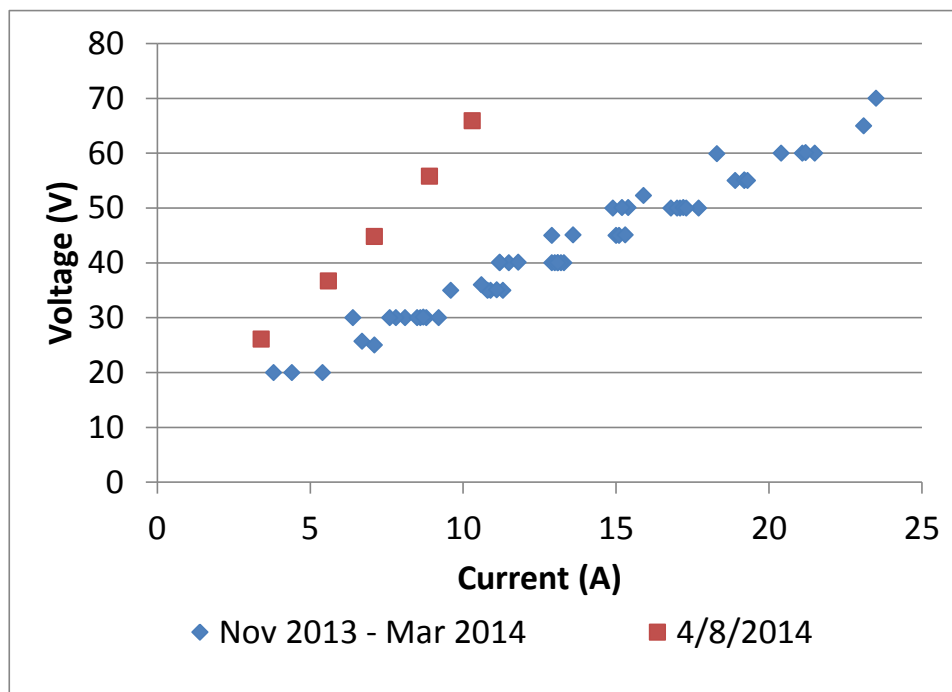


Figure 3.8: Measurement of EDM voltage and current on multiple dates in from October 2013 through March 2014



On April 8, 2014, the research team observed a significant increase in stack resistance as indicated by the data in Figure 3.9. We opened the stack to diagnose the cause and discovered the cathode had corroded badly, possibly because of a loose connecting wire. Corrosion of the cathode would cause the abnormally high resistance we observed. We also discovered several of the membranes in the mixed sodium concentrate compartments were scaled, which would also cause an increase in stack resistance.

**Figure 3.9: Stack resistance was abnormally high April 8, 2014. Upon inspection, the research team discovered a corroded cathode and scaled membranes in the mixed sodium concentrate compartment.**



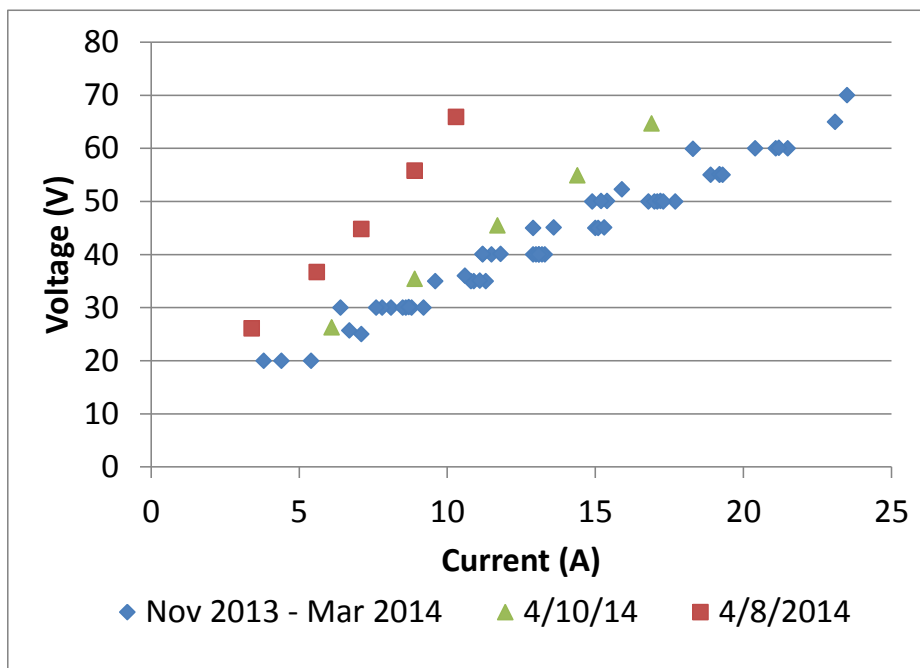
We replaced the corroded cathode and cleaned the membranes, replacing 26 membranes that appeared to have the heaviest scaling. The EDM stack was reinstalled on April 10, 2014 and tested to determine if stack resistance was restored to previously measured values.

The results of this test are shown in Figure 3.10. Stack resistance decreased significantly on April 10, 2014 but was still slightly higher than measurements recorded during testing up to this point. It is likely that some of the remaining membranes in the stack were scaled.

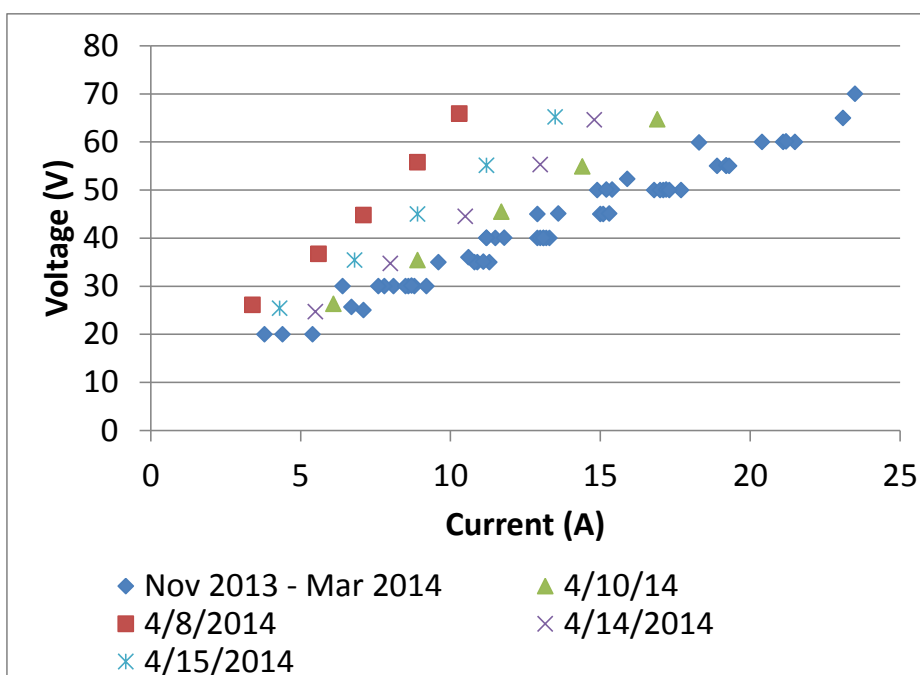
The research team continued to observe increase in stack resistance in subsequent measurements as shown in Figure 3.11. One explanation is operation of the stack at higher concentrate conductivities near the end of testing. The research team maintained conductivity in the mixed sodium concentrate stream below 40 mS/cm during the resistance measurements made shown in Figure 3.8. Near the end of testing we allowed conductivity in the mixed sodium concentrate to climb as high as 80 mS/cm. The data for the month of April 2014 shows the resistance steadily increasing. Higher concentrations of ions in the mixed sodium

concentrate stream at the end of testing were likely the cause of the membrane scaling and higher stack resistances observed.

**Figure 3.10: Stack resistance decreased after replacing the cathode and some of membranes but resistance was still higher than previous measurements.**



**Figure 3.11: EDM resistance increased in April 2014 when the research team tested the effect of operating with higher mixed sodium concentrate conductivity**

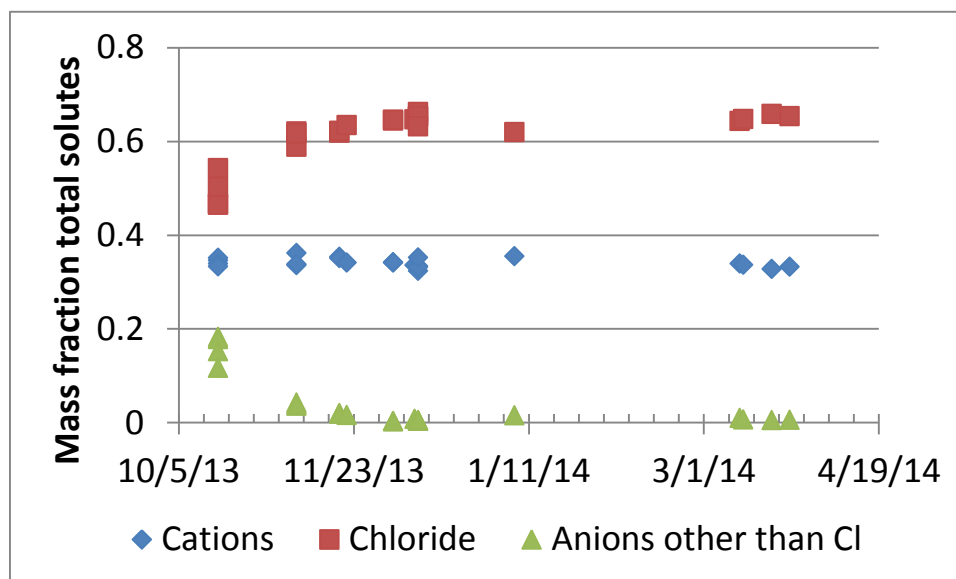


### 3.2.4 Experiment 4: Evaluation of EDM concentrate streams

EDM is designed to generate two concentrate streams of highly soluble salts. Ideally, the mixed chloride concentrate would contain only chloride and cations, and the mixed sodium concentrate would contain only sodium and anions, but leakage, imperfect membrane ion selectivity, impurities in the NaCl used, and other factors prevent the system from achieving perfect separation of ions in the two concentrate streams. The objective of this experiment was to evaluate how effectively EDM separated ions into chloride and cations in one concentrate stream and sodium and anions in the other.

Mass fraction of cations, chloride, and all anions other than chloride in the mixed chloride concentrate stream are shown in Figure 3.12. The data are from samples collected during operation from October 16, 2013 through March 25, 2014. On the first measurement on October 16, 2013, approximately 12 percent of the ions in the mixed chloride concentrate stream were anions other than chloride, comprised chiefly of 2,800 mg/L of sulfate. The sulfate concentration decreased until it was less than 100 mg/L in December. Anions other than chloride never comprised more than 2 percent of the total weight of ions after November 7, 2013.

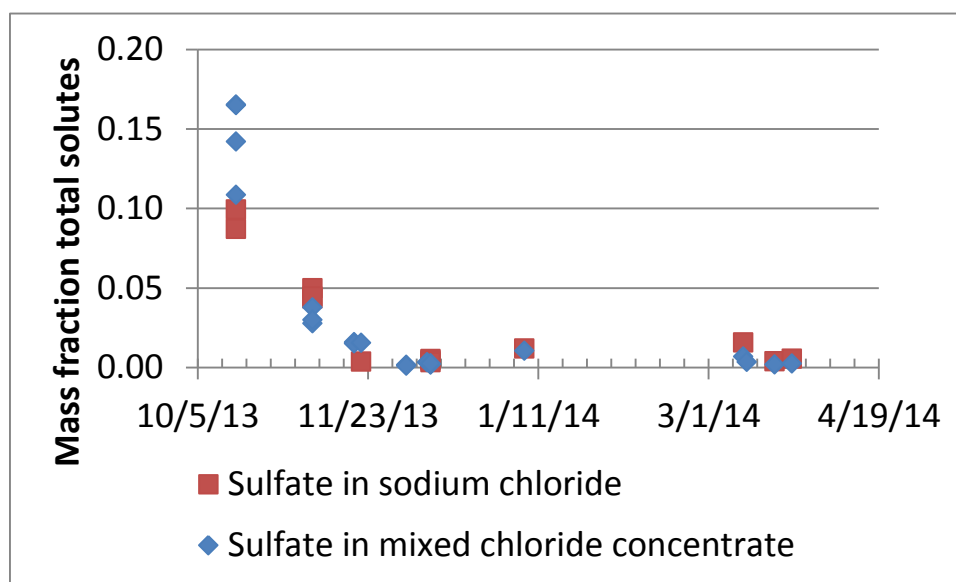
**Figure 3.12: Evaluation of Mixed Chloride Concentrate: Mass fraction of cations, chloride, and anions other than chloride.**



The cause for the high sulfate concentrations in the mixed chloride concentrate stream can be explained by the data in Figure 3.13 showing mass fraction of sulfate in the sodium chloride stream and in the mixed chloride concentrate stream during the same period. The NaCl stream contained 3,600 mg/L of sulfate the day sulfate in the mixed chloride concentrate stream measured 2,800 mg/L. Sulfate concentration in the NaCl stream decreased to 1,700 mg/L by the first week in November, then to less than 100 mg/L by the third week in November. This paralleled the decrease in sulfate in the mixed chloride concentrate stream over the same period. The research team was not aware of any cause of contamination of the NaCl stream with

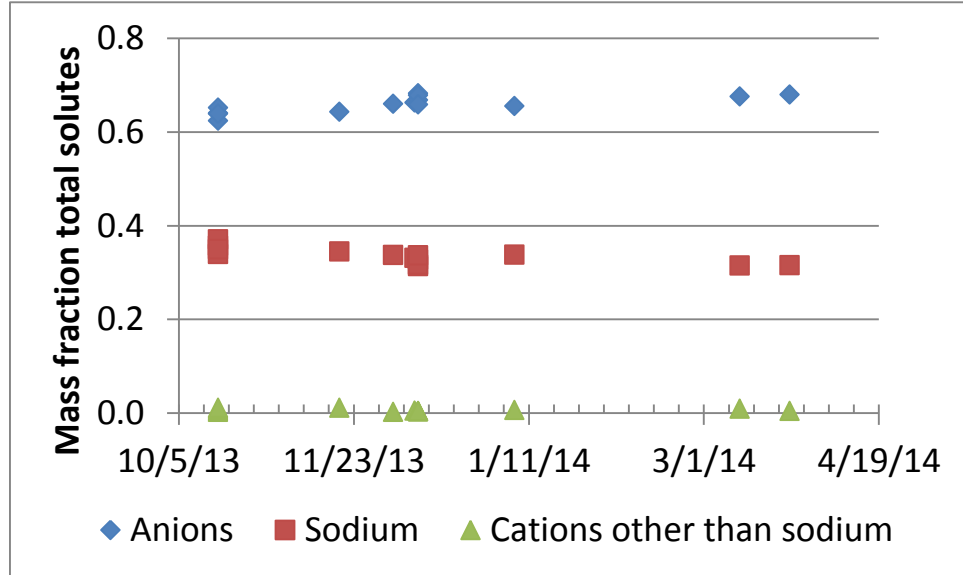
sulfate. The October 16, 2014 samples were the first collected, and therefore we have no evidence of how long or to what extent the elevated sulfate concentrations might have been present in the mixed chloride concentrate. It is evident, however, that contamination of the sodium chloride stream with sulfate led to contamination of the mixed chloride concentrate stream. EDM was conceived with monovalent selective membranes between the NaCl and concentrate streams to protect against contamination of the concentrate streams by divalent ions in the sodium chloride solution. The stack tested, however, was manufactured with regular rather than monovalent selective membranes.

**Figure 3.13: Mass fraction sulfate in the sodium chloride and mixed sodium concentrate streams.**



Mass fraction of anions, sodium, and all cations other than sodium in the mixed sodium concentrate stream in samples collected during operation from October 2013 through March 2014 are shown in Figure 3.14. Cations other than sodium were typically 1 percent or less of the total ions by weight.

**Figure 3.14: Evaluation of Mixed Sodium Concentrate: Mass fraction of anions, sodium, and cations other than sodium.**



### 3.2.5 Experiment 5: Evaluation of EDM relative transport numbers

Water quality data were collected several times during testing for calculation of RTN. Equations used for RTN calculations were as follows.

The methodology for calculating RTNs was described in Chapter 2. The transport of magnesium relative to sodium into the mixed chloride concentrate chamber is calculated as follows:

$$RTN_{Na}^{Mg} = \frac{flux\ Mg\ [Na]_d}{flux\ Na\ [Mg]_d}$$

The RTN for transport of calcium relative to sodium into the mixed chloride concentrate chamber was calculated as follows:

$$RTN_{Na}^{Ca} = \frac{flux\ Ca\ [Na]_d}{flux\ Na\ [Ca]_d}$$

The RTN for transport of sulfate relative to chloride into the mixed sodium concentrate chamber is calculated as follows:

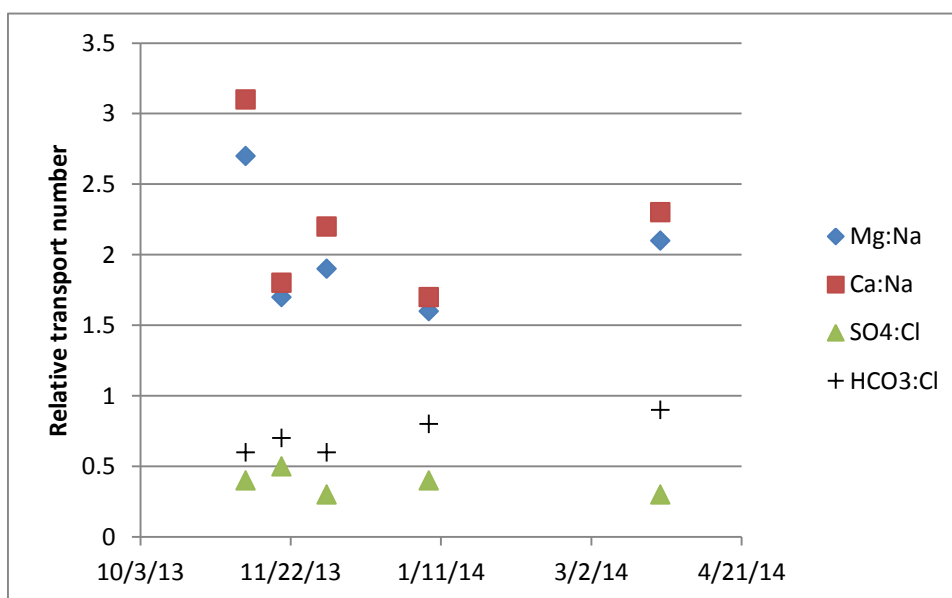
$$RTN_{Cl}^{SO4} = \frac{flux\ SO4\ [Cl]_d}{flux\ Cl\ [SO4]_d}$$

The RTN for transport of calcium relative to sodium into the mixed chloride concentrate chamber is calculated as follows:

$$RTN_{Cl}^{HCO3} = \frac{flux\ HCO3\ [Cl]_d}{flux\ Cl\ [HCO3]_d}$$

The results for RTN measurements are shown in Figure 3.13. There was a wider range in RTN values for the cations than for the anions. The RTN for magnesium to sodium transported into the mixed chloride concentrate stream ranged from 1.6 to 2.7. The average was 2.0. The RTN for calcium to sodium ions transported into the mixed chloride concentrate ranged from 1.7 to 3.1, and the average was 2.2. The RTN for sulfate to chloride transported into the mixed sodium concentrate stream ranged from 0.3 to 0.5, and the average was 0.4. The RTN for bicarbonate to chloride transported into the mixed sodium concentrate stream ranged from 0.6 to 0.9, and the average was 0.7.

**Figure 3.16: RTN values measured in Experiment 5**



### 3.2.6 Experiment 6: Evaluation of water transported across EDM membranes

The objective of Experiment 6 was to measure the amount of water transported across the membranes with ions. We conducted the experiment at different concentrations in the sodium chloride compartment to evaluate the effect of sodium chloride concentration on the rate of water transport. We also conducted the experiment at different voltages to evaluate the effect of current on water transport.

The results for Experiment 6 are shown in Table 3.3. The research team evaluated the effect of sodium chloride concentration on ion transport by conducting the experiment at three different conductivities in the sodium chloride compartment (25 mS/cm, 35 mS/cm, and 50 mS/cm). Stack voltages tested were 80 V, 135 V, and 152 V. Mixed sodium conductivities ranged between 27 and 58 mS/cm, and mixed chloride conductivities ranged between 37 and 81 mS/cm. Water transport into the mixed chloride concentrate ranged from 17 mole/eq to 21 mole/eq, and the average was 19.6 mole/eq., the mean 20 mole/eq, and the standard deviation 1.42. Water transported into the mixed sodium concentrate ranged from 19 mole/eq to 24 mole/eq, and the average was 20.7 mole/eq. The median was 20 mole/eq, and the standard deviation was 1.41.

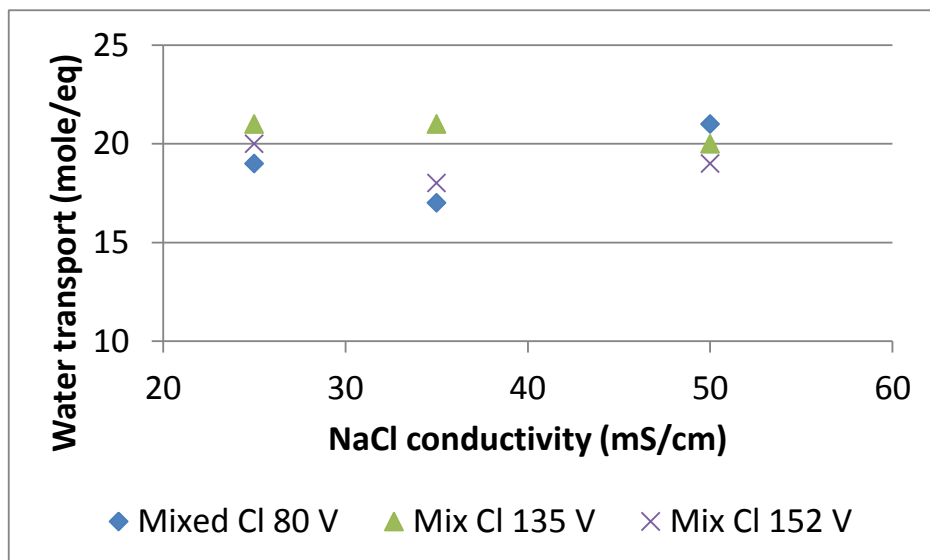


**Table 3.3: Experiment 6 results December 2013**

Trial	Conductivity (mS/cm)					Voltage (V)	Current (A)	Water transfer rate (mole/eq)	
	NaCl	EDM feed	EDM diluate	Mixed chloride	Mixed sodium			Mixed chloride	Mixed sodium
1	25	3.7	2.4	39 to 48	27 to 39	135	34	21	19
2	35	3.7	2.4	50 to 58	33 to 41	135	34	21	20
3	50	3.7	2.4	44 to 52	28 to 35	135	34	20	20
4	25	3.8	2.9	39 to 44	31 to 36	80	25	19	21
5	35	3.8	2.9	37 to 43	32 to 38	80	25	17	21
6	50	3.8	2.9	37 to 42	33 to 39	80	25	21	24
7	25	3.3	2.0	77 to 81	53 to 58	152	35	20	21
8	35	3.3	2.0	77 to 81	53 to 58	152	35	18	20
9	50	3.3	2.0	70 to 76	45 to 53	152	35	19	20
Average								19.6	20.7
Median								20	20
Standard Deviation								1.42	1.41

The effect of sodium chloride concentration and voltage on water transport into the mixed chloride concentrate is shown in Figure 3.17. There was no trend in the data to suggest that sodium chloride concentration or voltage had an effect on water transport into the mixed chloride concentrate stream.

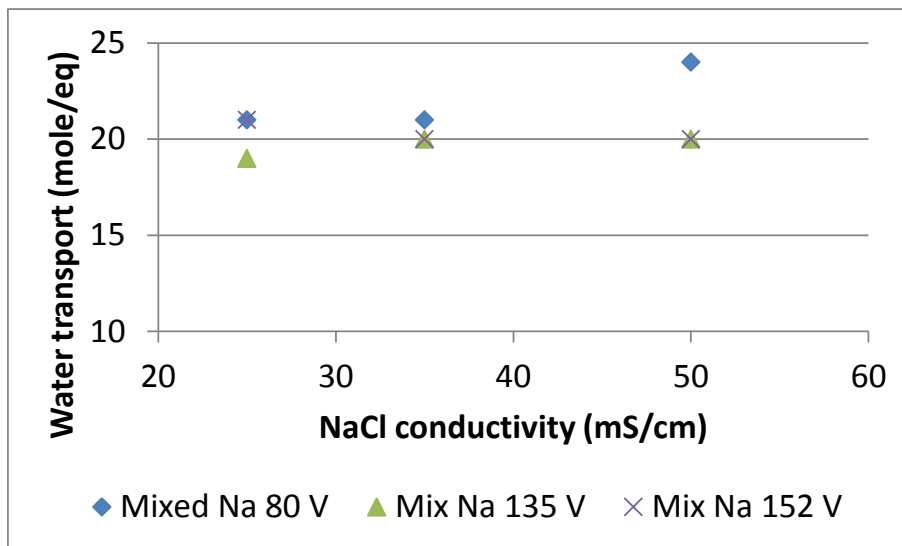
**Figure 3.17: Effect of sodium chloride compartment concentration effect on water transport into the mixed chloride stream.**



Sodium chloride compartment concentration and voltage had no observed effect on water transport into the mixed chloride concentrate stream.

The effect of sodium chloride concentration and voltage on water transport into the mixed sodium concentrate is shown in Figure 3.18. As with the mixed chloride concentrate, there was no trend in the data to suggest that sodium chloride concentration or voltage had an effect on water transport into the mixed sodium concentrate stream.

**Figure 3.18: Effect of sodium chloride compartment concentration on water transport into the mixed sodium concentrate stream.**



Sodium chloride compartment concentration and voltage had no observed effect on water transport into the mixed sodium concentrate stream.

We conducted Experiment 6 two more times during testing, once in January 2014 and again in April 2014, and the results are shown in Table 3.4. The objective was to see if any changes in water transport had occurred after further operation of the EDM stack. In previous testing, water transport rates ranged from 17 moles/eq to 21 moles/eq in the mixed chloride and from 10 moles/eq to 24 moles/eq in the mixed sodium. The mixed chloride water transfer rate was slightly greater than measured previously, and the mixed sodium water transfer rate was consistent. Overall there was no apparent difference in water transport rates.

**Table 3.4: Experiment 6 results in January and April 2015**

Trial	Conductivity (mS/cm)					Voltage (V)	Current (A)	Water transfer rate (mole/eq)	
	NaCl	EDM feed	EDM diluate	Mixed chloride	Mixed sodium			Mixed chloride	Mixed sodium
1/8/14	51	3.0	1.9	120	60	135	26	23	20
4/15/14	35	2.7	1.7	120	60	145	27	22	20

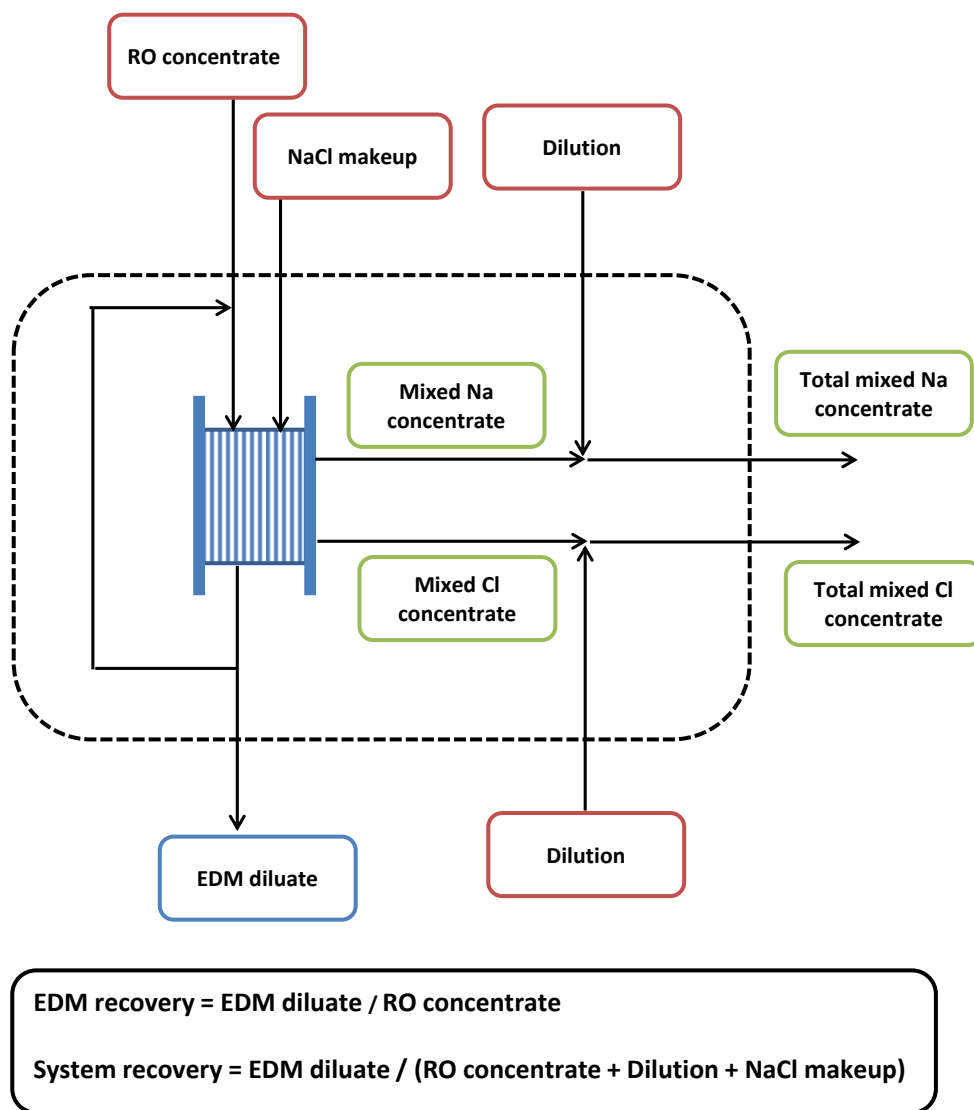
### 3.2.7 Experiment 7: Evaluation of EDM recovery

Recovery for EDM and for the system as a whole were calculated as described in Section 2.2.7 and the mass diagram is repeated here as Figure 3.19 for convenience. The research team conducted Experiment 7 three times during testing.

We held voltage constant to meet the EDM treatment goal while we measured dilution water consumption and EDM flows and conductivities. We set the dilution rate to maintain mixed sodium concentrate conductivity below 60 mS/cm. No dilution water was added to the mixed sodium concentrate because salts with potential to precipitate in the mixed chloride concentrate have higher solubilities. The research team calculated concentrate flows using the water transport rate measured in Experiment 6, 20 mole/eq, which is equal to 0.36 L/eq.

The results of this experiment are shown in Table 3.5. EDM recoveries in the three trials were 96 percent, 98 percent, and 97 percent. Conductivity in the mixed sodium concentrate was maintained around 36 mS/cm in the trial with 96 percent recovery. The overall system recoveries in the three trials ranged from 91 percent to 92 percent. It is evident that EDM recovery depends in part on the amount of dilution water used to maintain set points in the two concentrate streams. Without including dilution water in the calculation, total system recovery would have ranged from 93 percent to 96 percent.

Figure 3.19: Water mass balance diagram for calculation of EDM recovery.



**Table 3.5: Experiment 7 results and calculation of EDM recovery**

	3/19/14	3/24/14	4/1/14
Elapsed time (min)	1621	1391	2746
EDM feed normality (meq/L)	28	29	34
EDM diluate normality (meq/L)	10	10	10
Mixed Na conductivity (mS/cm)	61	53	36
Mixed Cl conductivity (mS/cm)	116 to 143	42 to 139	95 to 148
Dilution water used Mixed Na (L)	1170	1802	3687
Dilution water used Mixed Cl (L)	0	0	0
Total dilution water used (L)	1170	1802	3687
NaCl makeup water (L)	868	476	590
Total eq transferred during treatment (eq)	2411	1322	4373
EDM concentrate excluding dilution (L)	1736	952	1179
EDM feed (RO concentrate) (L)	38,800	39,496	39,496
EDM diluate (L)	37,042	38,545	38,317
EDM recovery (%)	96	98	97
Total system recovery (%)	91	92	92

### 3.2.8 Experiment 8: Treatment of the EDM concentrate streams

The research team conducted experiments to treat EDM concentrate by precipitation and by electrodialysis.

#### 3.2.8.1 *Mixing EDM concentrate streams without chemical addition*

The research team mixed the EDM concentrate streams shown in Tables 3.6, 3.7, and 3.8 in three trials to observe the extent of divalent ion removal without chemical addition. We mixed the blended concentrate volumes for two hours and collected samples periodically during mixing to evaluate the effect of mixing time. The samples were filtered through a 1 µm bag filter and shipped to the laboratory for analyses.

**Table 3.6: Experiment 8, Trial 1 conditions**

<b>Stream</b>	<b>pH</b>	<b>Ca (mg/L)</b>	<b>Mg (mg/L)</b>	<b>Na (mg/L)</b>	<b>SO<sub>4</sub> (mg/L)</b>	<b>HCO<sub>3</sub> (mg/L)</b>	<b>Cl (mg/L)</b>	<b>TDS (mg/L)</b>
Mixed sodium concentrate	7.8	700	430	14,000	11,000	19,000	19,000	61,000
Mixed chloride concentrate	7.3	4100	2800	12,000	2000	2300	32,000	60,000

**Table 3.7: Experiment 8, Trial 2 conditions**

<b>Stream</b>	<b>pH</b>	<b>Ca (mg/L)</b>	<b>Mg (mg/L)</b>	<b>Na (mg/L)</b>	<b>SO<sub>4</sub> (mg/L)</b>	<b>HCO<sub>3</sub> (mg/L)</b>	<b>Cl (mg/L)</b>	<b>TDS (mg/L)</b>
Mixed sodium concentrate	8.3	210	110	24,000	11,000	17,000	20,000	63,000
Mixed chloride concentrate	7.2	6500	4300	11,000	210	320	42,000	79,000

**Table 3.8: Experiment 8, Trial 3 conditions**

<b>Stream</b>	<b>pH</b>	<b>Ca (mg/L)</b>	<b>Mg (mg/L)</b>	<b>Na (mg/L)</b>	<b>SO<sub>4</sub> (mg/L)</b>	<b>HCO<sub>3</sub> (mg/L)</b>	<b>Cl (mg/L)</b>	<b>TDS (mg/L)</b>
Mixed sodium concentrate	8.5	140	78	23,000	12,000	15,000	18,000	57,000
Mixed chloride concentrate	7.0	5500	3900	14,000	170	200	42,000	67,000

The results of Trials 1, 2, and 3 are shown in Figures 3.20, 3.21, and 3.22. The fraction remaining of each ion is plotted against mixing time. From the data, it is clear calcium carbonate was the primary precipitate during these trials. Calcium fractions remaining ranged between 0.46 and 0.73, and bicarbonate fractions remaining ranged between 0.24 and 0.66. Magnesium and sulfate were not removed by mixing the two concentrate streams. The pH did not exceed 7.6 during any of the measurements, and calcium and bicarbonate removal increased with mixing time. The percentage of calcium removed was greatest in the sample with greatest initial calcium concentration and least in the sample with the smallest initial calcium concentration.

The research team checked the observed results against results predicted with the MINTEQ software program. MINTEQ is a chemical equilibrium software used to determine speciation of ions. An ion is dependant on other ions in solution as well as pH of the solution. For this project

the program predicted calcium carbonate precipitation and no calcium sulfate precipitation as observed in the trials. MINTEQ, however, also predicted some precipitation of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), but magnesium removal was not observed in the trials.

**Figure 3.20: Fractions of ions remaining after mixing the EDM concentrate streams without chemical addition in Trial 1**

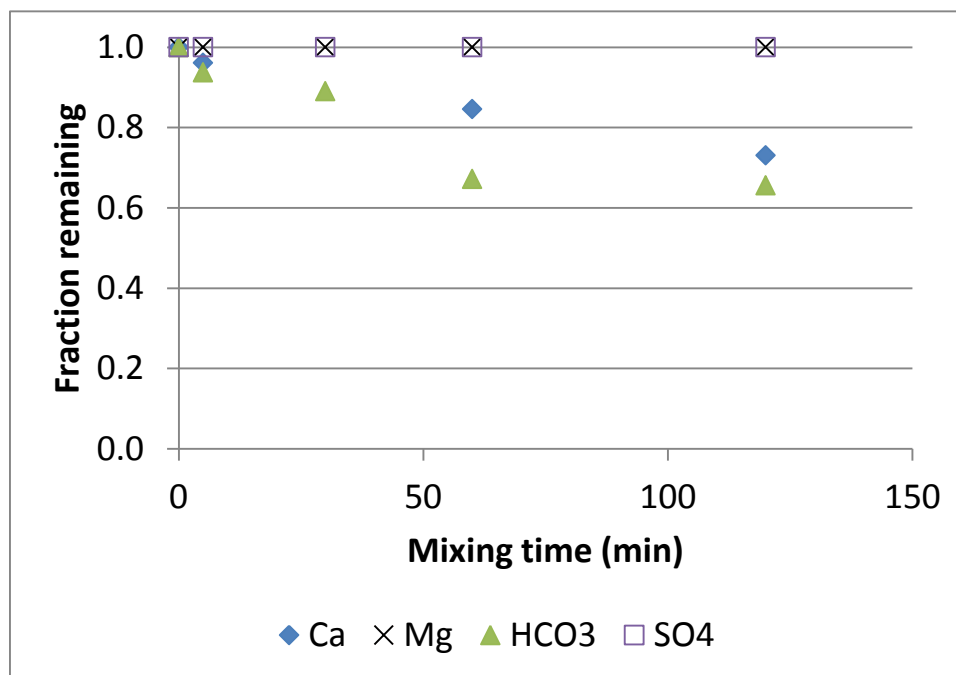


Figure 3.21: Fractions of ions remaining after mixing the EDM concentrate streams without chemical addition in Trial 2

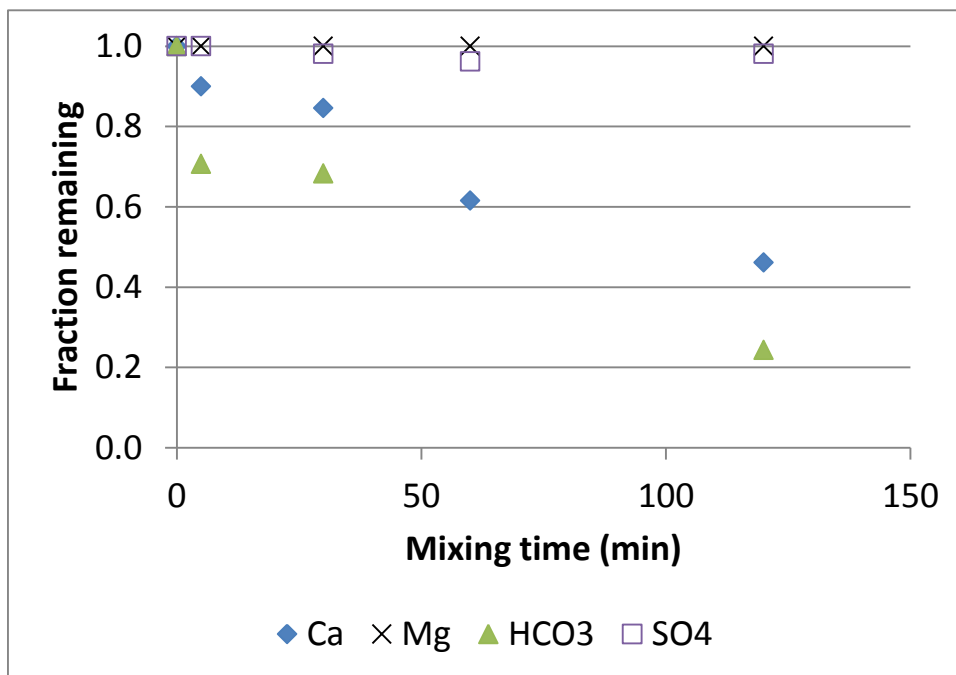
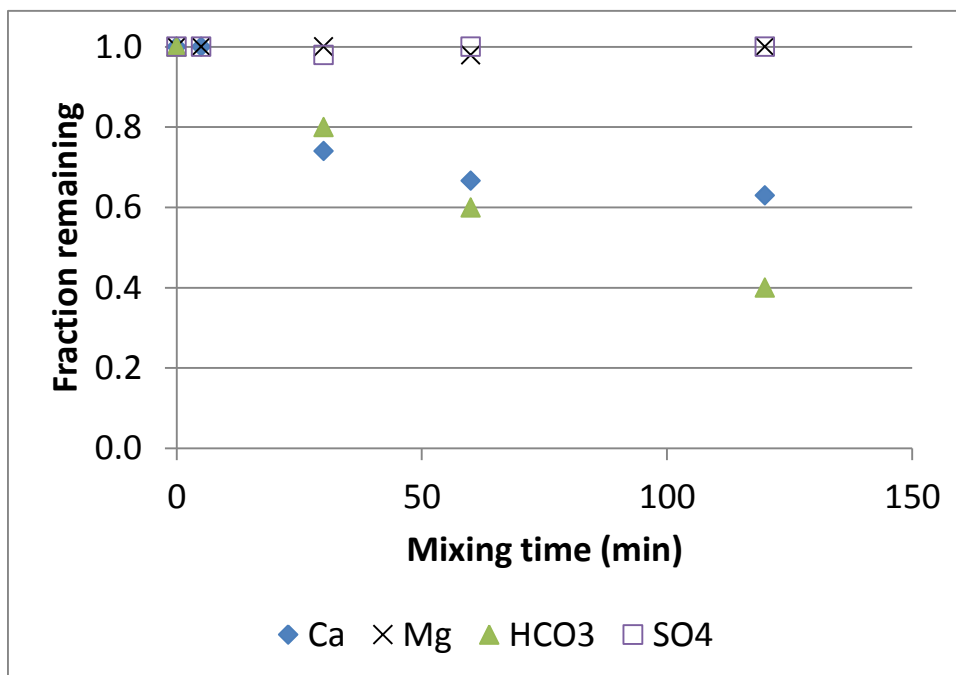


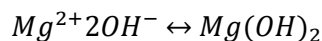
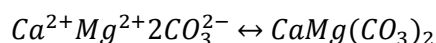
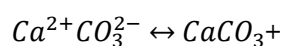
Figure 3.22: Fractions of ions remaining after mixing the EDM concentrate streams without chemical addition in Trial 3





### 3.2.8.2 Mixing EDM concentrate streams with sodium hydroxide addition

Precipitation of calcium carbonate, magnesium hydroxide, and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) occur in the following pH dependent reactions. Precipitation of calcium carbonate and dolomite increases as pH increases because carbonate speciation shifts from bicarbonate to carbonate. Magnesium precipitation as magnesite ( $\text{Mg}(\text{OH})_2$ ) increases as pH increases because hydroxide ( $\text{OH}^-$ ) concentrations increase. The research team tested sodium hydroxide addition to raise pH and increase removals of calcium and magnesium.

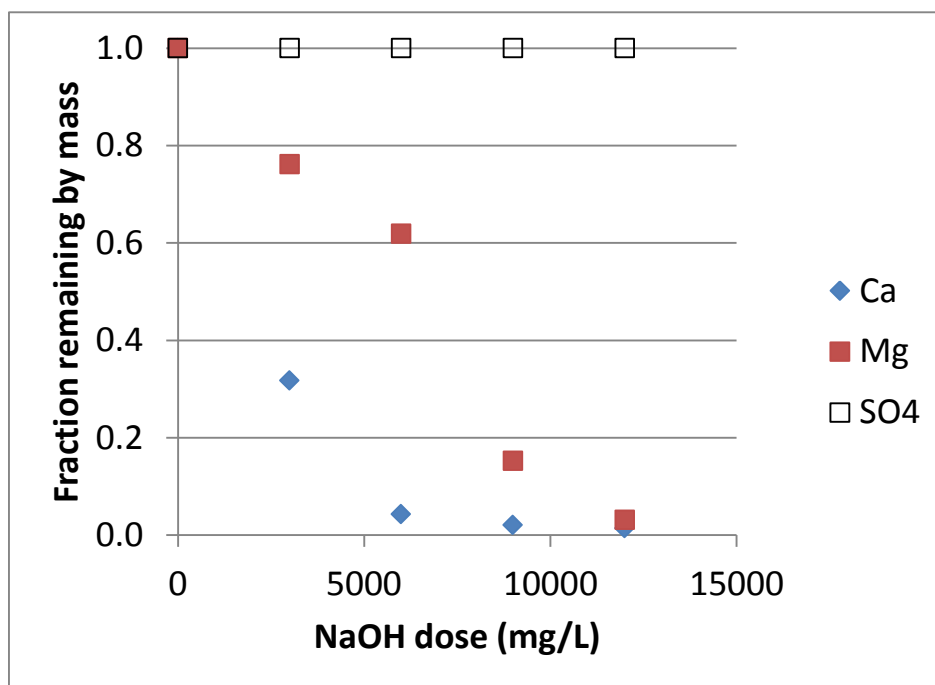


The research team conducted the experiments with chemical addition using four NaOH doses (3,000 mg/L, 6,000 mg/L, 9,000 mg/L, and 12,000 mg/L) and a blank (no NaOH added). After NaOH addition, the samples were mixed for 5 minutes then allowed to settle. The settled sample was filtered through a 0.45  $\mu\text{m}$  filter.

The results of the trial with NaOH addition are shown in Figure 3.23 as mass fraction remaining. Calcium and magnesium were removed from the samples but sulfate was not. At a dose of 3,000 mg/L NaOH, calcium was reduced by 70 percent and magnesium by 24 percent. The settled water pH was 8.5. At a NaOH dose of 6,000 mg/L NaOH, calcium was reduced by 96 percent and magnesium by 38 percent, and the pH was 9.2. At 9,000 mg/L NaOH, calcium was reduced by 98 percent and magnesium by 85 percent. The pH was 10.0. At the 12,000 mg/L NaOH dose, 99 percent of calcium and 97 percent of magnesium were removed. The pH was 10.0.

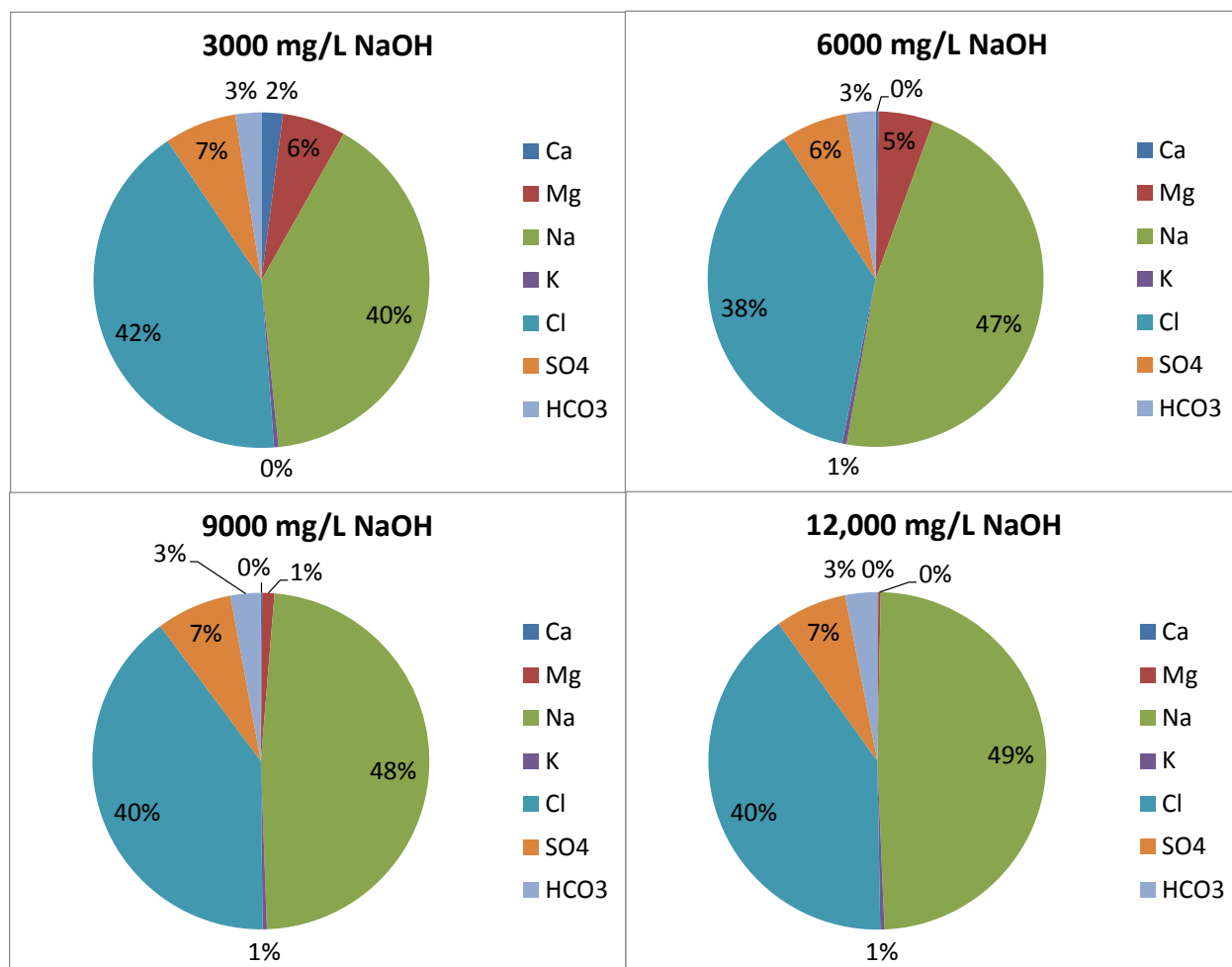
The solubility of calcium sulfate is about 2,400 mg/L, so the blended solutions should have been supersaturated in calcium sulfate. There was, however, no evidence of precipitation of calcium sulfate. The reason appears to be that calcium carbonate precipitated first and reduced the calcium content below the saturation level of calcium sulfate. The minimum solubility of calcium carbonate is only 15 mg/L, compared to a solubility of 2,400 mg/L for calcium sulfate. Moreover, calcium sulfate tends to have slower kinetics of precipitation, and it can remain in a supersaturated condition for extended periods.

**Figure 3.23: Mass fraction of ions remaining after mixing the EDM concentrate streams with NaOH in Trial 4**



Composition of the filtered samples is shown in Figure 3.24. The graphs show the percentage of total meq for each ion. As NaOH dose increased from 3,000 mg/L to 12,000 mg/L, the percentage of the charges contributed by sodium and chloride increased from 82 percent to 89 percent as the percentage of charges contributed by calcium and magnesium decreased from 8 percent to less than 0.5 percent.

**Figure 3.24: Percentage of total meq for each ion after blending and NaOH addition**

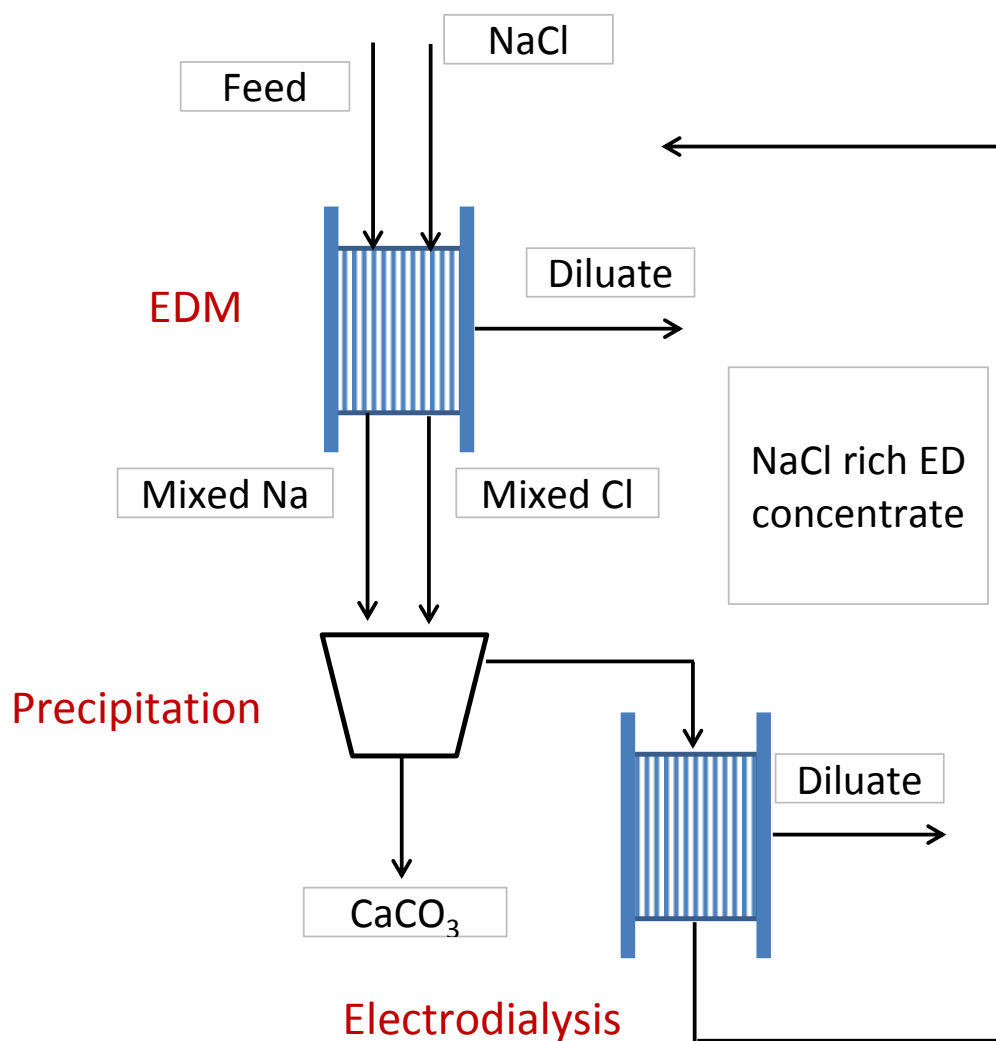


### 3.2.9 Experiment 9: Treatment of EDM concentrate streams with electrodialysis

The objective of Experiment 9 was to evaluate recovery of sodium chloride from the EDM concentrate. Sodium chloride consumption represents a significant operation cost, and therefore recovery of sodium chloride from EDM concentrate has potential to significantly reduce the cost for EDM treatment. The supernatant from the precipitation step was treated in an electrodialysis stack containing monovalent ion-selective membranes.

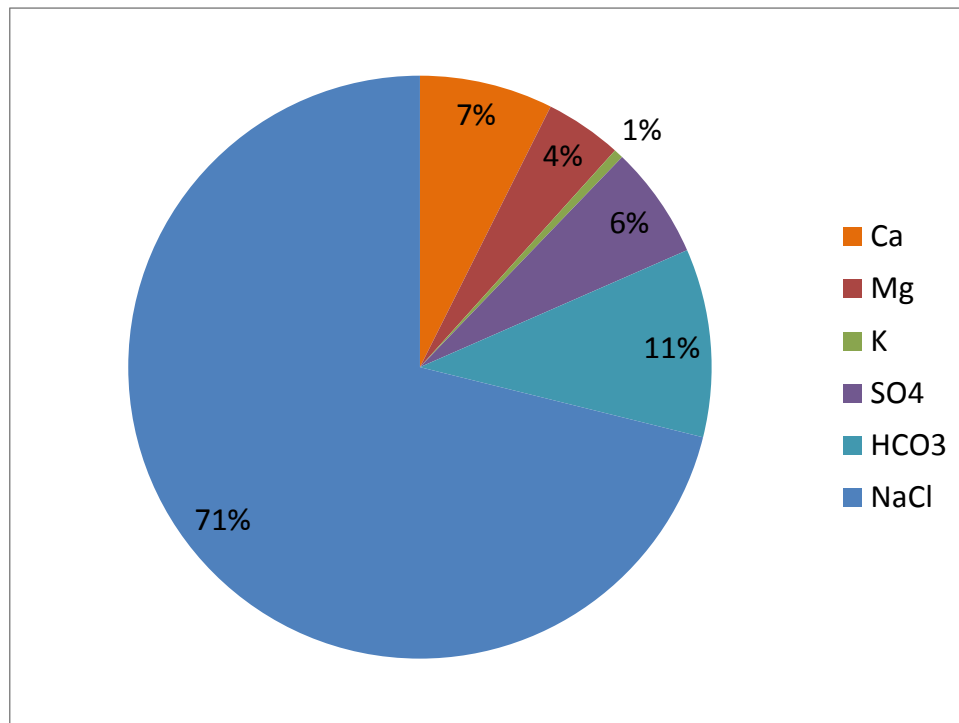
The method tested is shown in Figure 3.25. The two EDM concentrate streams were combined and treated with sodium hydroxide. We selected a 6,000 mg/L NaOH dose because this dose reduced calcium to 120 mg/L in Experiment 8, and higher doses yielded diminishing returns for calcium removal. Supernatant from the precipitation step was fed to the ED with monovalent ion-selective membranes. The ED feed solution was recirculated until conductivity in the ED concentrate approached 200 mS/cm.

**Figure 3.25: Treatment of EDM concentrate in Experiment 9 by precipitation and electro dialysis with monovalent ion-selective membranes.**



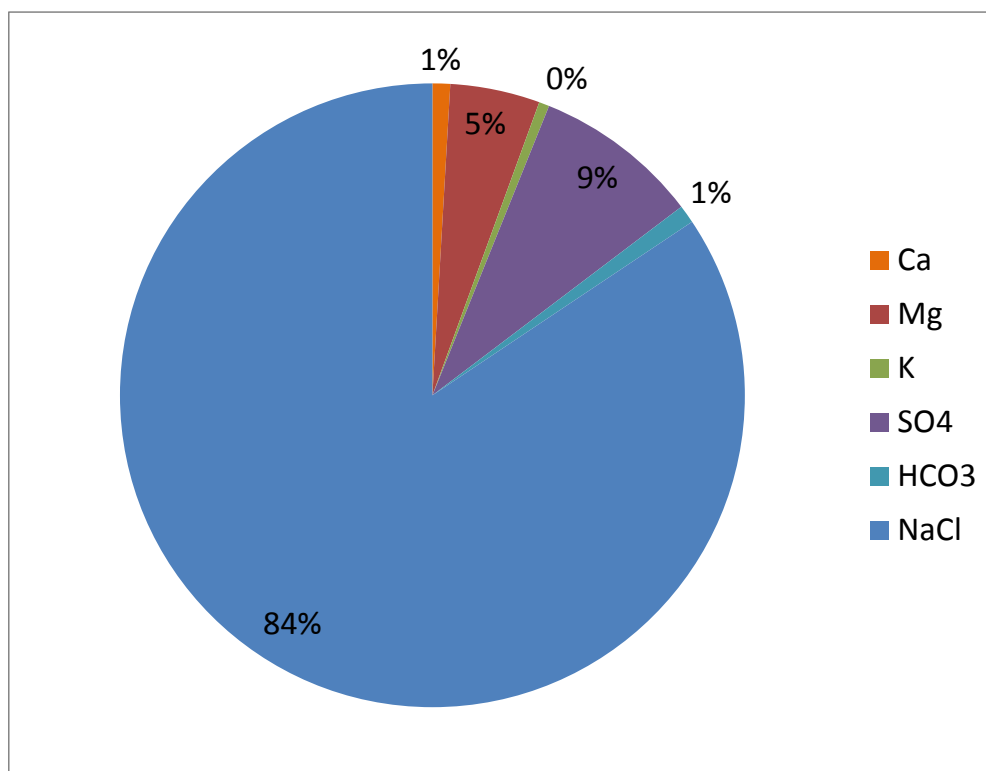
The composition of the blended EDM concentrate by mass before the precipitation step is shown in Figure 3.26. The blend of the EDM mixed sodium and mixed chloride concentrate streams was 71 percent sodium chloride by mass and 29 percent other ions.

**Figure 3.26: Composition by mass of the blended EDM concentrate stream before the precipitation treatment step.**



The composition of EDM after it was treated in the precipitation step is shown in Figure 3.27. The blended EDM concentrate was treated with 6,000 mg/L of sodium hydroxide. After the precipitation of calcium carbonate, the EDM concentrate blend was of the EDM mixed sodium and mixed chloride concentrate streams was 84 percent sodium chloride by mass and 16 percent other ions.

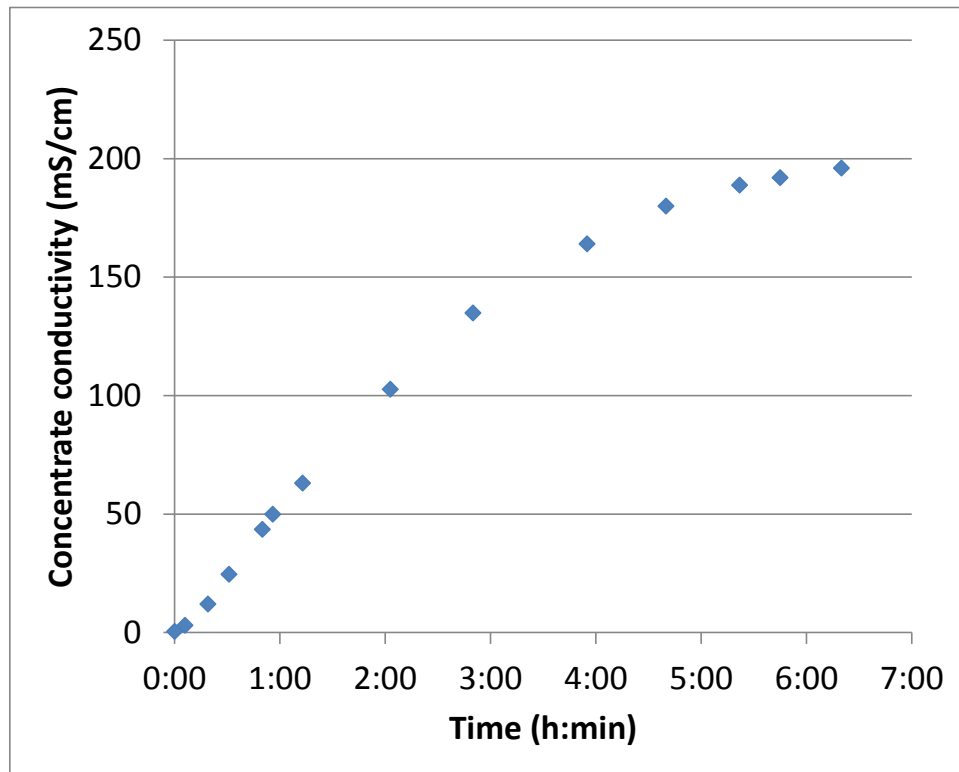
**Figure 3.27: Composition of the blended EDM concentrate stream after the precipitation treatment step using 6,000 mg/L.**



We transferred supernatant from the precipitation step to the ED feed tank. The treated EDM concentrate was recirculated through the ED for 6 hours and twenty minutes. Voltage in the stack ranged between 7 and 7.5 volts. Stack current was 0.5 amperes (A) at the start beginning and 6 A when the experiment was stopped.

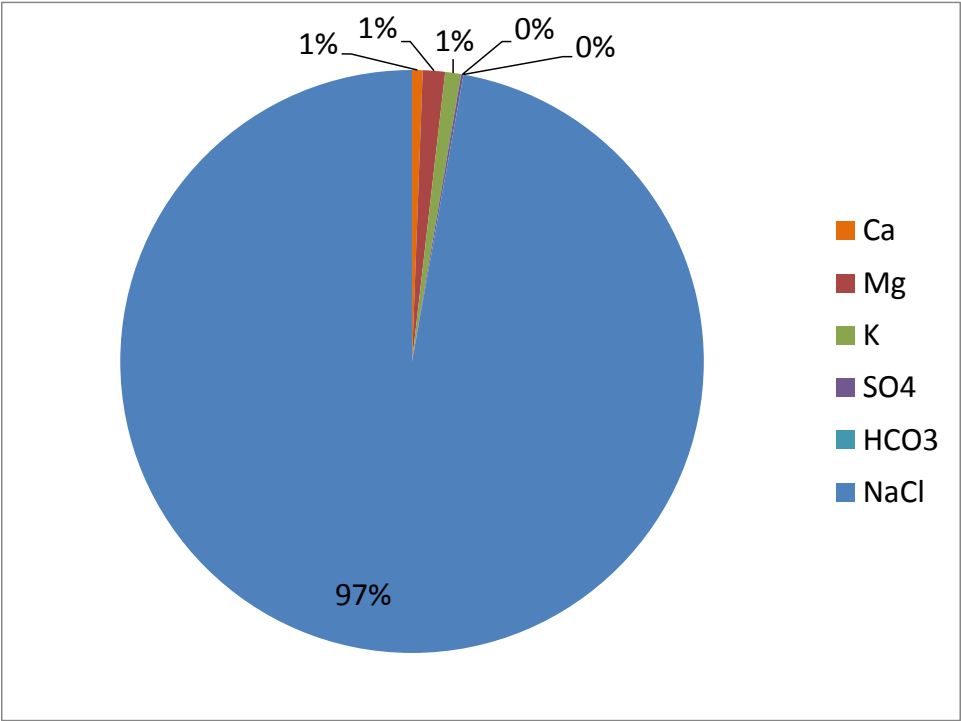
Conductivity of the ED concentrate stream during the experiment is shown in Figure 3.28. The experiment started with the ED concentrate compartment filled with RO permeate and a conductivity less than 0.1 mS/cm. Conductivity increased to 196 mS/cm over the 6 hour and 20 minute run time.

**Figure 3.28: Conductivity in the electrodialysis concentrate.**



Composition of the ED concentrate at the end of the experiment is shown in Figure 3.29. At the end of the experiment, the ED concentrate was 97 percent sodium chloride by mass and 3 percent other ions. Therefore, treatment of the EDM concentrate by precipitation with sodium hydroxide followed by electrodialysis with monovalent ion-selective membranes increased the percentage of sodium chloride in the blended concentrate from 71 percent to 97 percent by mass.

Figure 3.29: Composition of the ED concentrate at the end of the experiment by percent mass.





## CHAPTER 4: Full-scale Evaluations

### 4.1 Approach

Utilities considering applying this technology will be interested in full-scale costs and energy requirements. The research team used results from the full-scale stack demonstration to project treatment costs and energy requirements for the following three treatment plants:

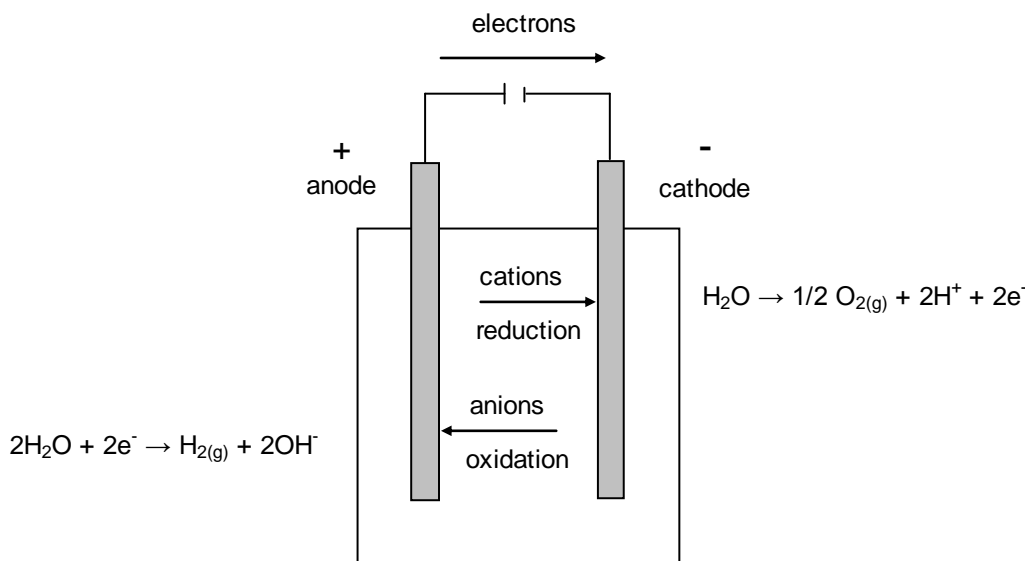
- The City of Beverly Hills Water Treatment Facility
- The Rancho California Water District Santa Rosa Water Reclamation Facility
- The City of Santa Monica Arcadia Water Treatment Plant

These evaluations were conducted in coordination with the City of Beverly Hills, the City of Santa Monica, and the Rancho California Water District. The utilities provided water quality data and operating data used in our evaluations. The research team modeled full-scale treatment at the three plants to calculate power requirements and treated water quality. The calculations were used to project treatment costs. We calibrated the model using the Beverly Hills test results.

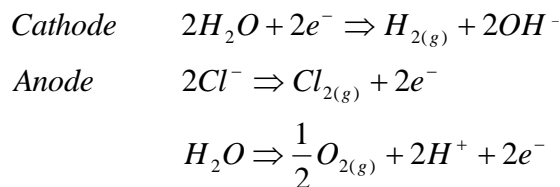
#### 4.1.1 Model description

A basic electrolytic cell is shown schematically in Figure 4.1. The cell comprises a cathode and anode in an electrolyte solution with a connection to an external power source. Current is carried by ions in electrolyte solutions and by electrons in the electrodes. Electrons are supplied to the cathode by the external power source and impart a negative charge to the cathode. The electrical potential difference between the cathode and anode causes cations to be drawn to the cathode and anions to be drawn to the positively charged anode.

**Figure 4.1: Schematic of a basic electrolytic cell.**



The key function of the electrodes is the efficient transfer of electrons between the electrolyte solution and the metal conductors of the electrodes through oxidation-reduction reactions. Electrons are transferred from anions in solution to the anode in an oxidation reaction. This is coupled with the transfer of electrons from the cathode to cations in solution in reduction reactions. For example, when NaCl is the electrolyte solution, water can be reduced at the cathode to form hydrogen gas and hydroxide ions, and chloride and water can be oxidized at the anode to form chlorine gas, oxygen gas, and hydrogen ions.



The rate of ion transport in solution is determined by thermodynamic and kinetic properties of the system. Thermodynamic properties are expressed by the driving forces that must be applied to transport the ions. Parameters that determine kinetic properties of the system are the diffusion coefficients of ions and the electric conductivity of the solution.

The driving force for ion transport in ED is an electrochemical potential gradient that is the sum of chemical and electrical potential gradients. Chemical potential gradients are the result of differences in concentration and pressure, and they exert a driving force for ion transport by diffusion. The change in chemical potential for an ion in solution at constant temperature can be expressed as

$$\frac{d\mu_i}{dx} = V_i \frac{dp_i}{dx} + RT \frac{d \ln(a_i)}{dx}$$

where  $\mu$  is chemical potential,  $V$  is the partial molar volume,  $p$  is pressure,  $x$  is distance in the direction of diffusion,  $R$  is the universal gas constant,  $T$  is absolute temperature, and  $a$  is ion activity. The change in electrochemical potential is

$$\frac{d\eta_i}{dx} = V_i \frac{dp_i}{dx} + RT \frac{d \ln(a_i)}{dx} + z_i F \frac{dU}{dx}$$

where  $\eta$  is electrochemical potential,  $z$  is ionic charge,  $F$  is Faraday's constant, and  $U$  is electrical potential.

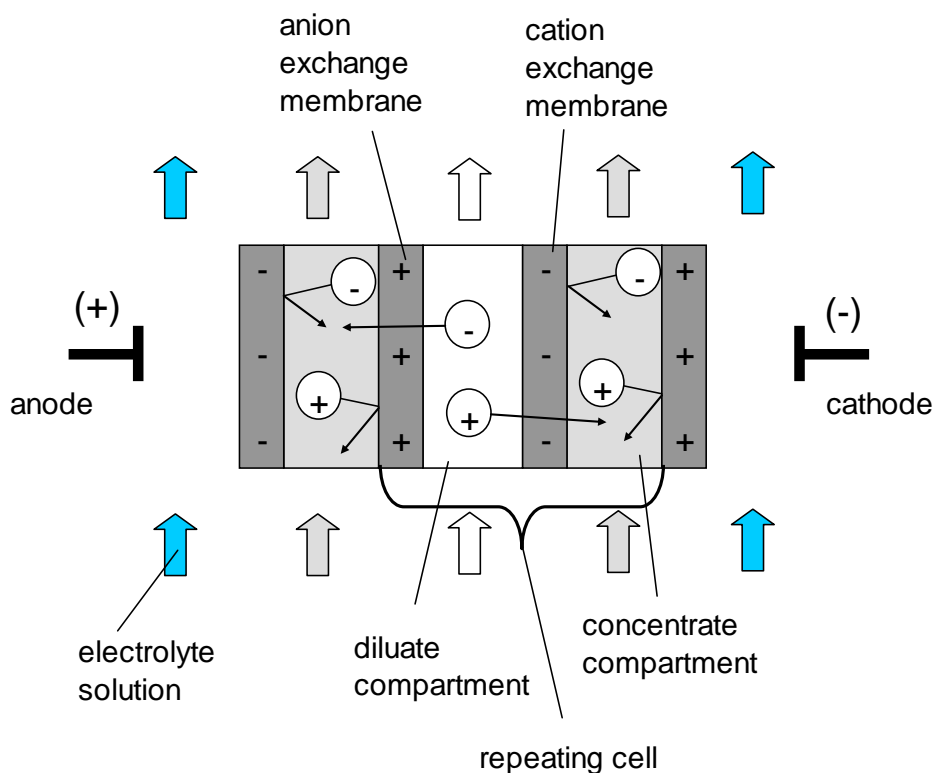
Equilibrium between two solutions separated by a membrane occurs when the electrochemical potentials of all species that can be exchanged are equal. This means two solutions separated by an ion exchange or reverse osmosis membrane can be in equilibrium even if they have different

chemical potentials, electrical potentials, or pressures, as long as the differences compensate for one another.

$$\eta_1 = \eta_2 = \mu_1 + FU_1 = \mu_2 + FU_2$$

A basic electrodialysis cell pair is illustrated in Figure 4.2. The cell pair comprises from left to right: a diluate compartment, an anion selective membrane, a concentrate compartment, and a cation selective membrane. A full-scale stack contains hundreds of such cell pairs between a cathode and anode.

**Figure 4.2: Schematic of an electrodialysis cell pair**



An ED stack comprises hundreds of ED cell pairs between electrodes. For ion transport to occur in an ED stack, the driving force must be sufficient to overcome friction forces that occur between the transported ions and surrounding water molecules or membrane matrix. These friction forces are expressed as resistances. The transport of ions in the electrodialysis stack results in a current that can be described by Ohm's law where  $U$  is voltage drop (V),  $I$  is current (A), and  $R$  is resistance (ohms).

$$U = IR$$

Current is carried by ions in electrolytic solutions. The theoretical current in an electrodialysis stack can be calculated by Faraday's law where  $q$  is flow, and  $\Delta N$  is change in normality in the diluate.

$$I_{theory} = Fq\Delta N$$

In practice, not all of the current flowing through an electrodialysis stack is associated with the transport of ions. The ratio of the theoretical current ( $I_{theory}$ ) to the actual current ( $I_{actual}$ ) is defined as the current utilization,  $\xi$ .

$$\xi = \frac{I_{theory}}{I_{actual}} = \frac{\Delta N_{theory}}{\Delta N_{actual}}$$

Current density,  $i$  (A/cm<sup>2</sup>), is current per unit of membrane cross-sectional area,  $A_m$  (cm<sup>2</sup>).

$$i = \frac{I}{A_m}$$

Resistance is a function of area resistance,  $r$  (ohm cm), distance,  $L$  (cm), and membrane cross-sectional area.

$$R = r \frac{L}{A_m}$$

The reciprocal of resistance is conductance, which has units of ohm<sup>-1</sup> or Siemens (S). The reciprocal of area resistance is specific conductance,  $k$  (S cm<sup>-1</sup>), also referred to as conductivity.

$$k = \frac{1}{r}$$

Specific conductance of an electrolyte solution depends on the concentration, charge, and mobility of ions in solution where  $z$  is ionic charge,  $v$  is stoichiometric coefficient,  $u$  is mobility (cm<sup>2</sup> s<sup>-1</sup> V<sup>-1</sup>), and  $C$  is molar concentration, all referring to ion  $i$ .

$$k = f(z_i v_i u_i C_i F)$$

Consequently, ion flux,  $J$ , can be expressed as

$$J = f(z_i v_i u_i C_i F \Delta U)$$

Equivalent conductance,  $\Lambda$  (cm<sup>2</sup> eq<sup>-1</sup> ohm<sup>-1</sup>), expresses the specific conductance contributed by one equivalent of ions in one liter of solvent where  $N$  is normality (eq L<sup>-1</sup>).

$$\Lambda = \frac{k}{N}$$

Ion exchange membranes play a key role in the transport and separation of ions. Typical ion exchange membranes used in ED have a polymer matrix with attached fixed ionic charges. Anion exchange membranes carry positive fixed charges and cation exchange membranes carry

negative fixed charges. Mobile ionic charges are associated with the fixed charges. Cations pass through the negatively charged cation exchange membrane while anions are repelled by Coulomb forces. Similarly, anion exchange membranes are selectively permeable to anions and exclude cations. Ions opposite in charge to the membrane are referred to as counterions, and those with like charge are referred to as co-ions.

Current is carried by cations and anions in electrolyte solutions, but different ions carry different portions of the current depending on their concentration, charge, and mobility. In general, divalent ions carry a higher percentage of current because they have a smaller hydration shell and greater charge. The fraction of current carried by a specific ion is described by its transport and transference numbers.

The fraction of total current carried by a specific ion is referred to as its transport number,  $t_i$ .

$$t_i = \frac{z_i J_i}{\sum_i z_i J_i}$$

The sum of all transport numbers is one. The transport numbers of anions and cations in solution do not differ significantly. In the membranes, however, transport is dominated by counterions. For ideally permaselective membranes, co-ions are completely excluded, the transport number for counterions is one, and the transport number for co-ions is zero. In practice, membrane counterion transport numbers are very close to one, and current in ED stacks is carried predominantly by counterions.

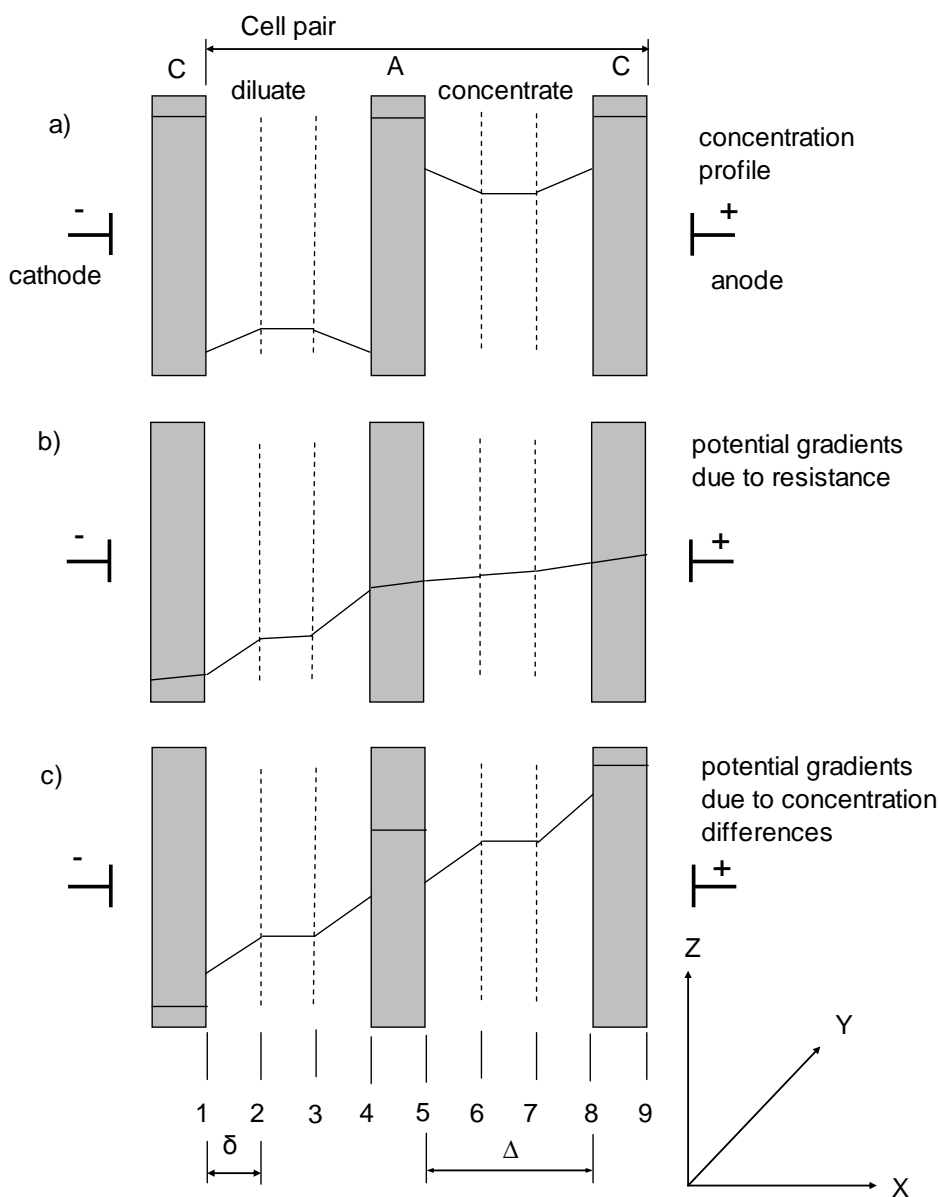
Ions are transported much faster through the membranes than they are through solution. This difference in transport rates leads to a depletion of ions at the membrane surface in the diluate and an accumulation of ions at the membrane surface in the concentrate. Hence, concentrations increase in the diluate and decrease in the concentrate across the boundary layer from the membrane surface to the bulk solution. Ion concentrations are considerably higher in the membranes than in solution to balance membrane fixed charges, and these ions are almost exclusively counterions.

Because current in electrolyte solutions is carried by ions, a limiting current density ( $i_{lim}$ ) is reached when the concentration of ions available to transfer current approaches zero in the diffusion boundary layer on the feed side of the membrane. At  $i_{lim}$ , increases in voltage do not increase current density until voltage is high enough to split water molecules into  $H^+$  and  $OH^-$ . After water splitting occurs, current is carried by  $H^+$  and  $OH^-$  ions. Operation of ED near the limiting current density must be avoided because the pH extremes caused by water splitting can damage the membranes and cause precipitation of pH sensitive salts.

Figure 4.3 is a schematic representation of concentration gradients and potential gradients across the cell pair at a point along the Y-axis. Concentrate and diluate flows are co-current in the Y direction, and the figure shows a cross-section of the cell pair through the X-Z plane. The electrodes generate an electric potential difference in the X direction, perpendicular to the membranes.

Ion transport in the X direction occurs by two mechanisms: 1) migration driven by the electrical potential gradient and 2) diffusion driven by chemical potential gradients due to concentration differences. Ion flux by diffusion is negligible relative to migration and can be accounted for within the current utilization factor. Nevertheless, the electromotive force exerted by the diffusion potential must be counteracted by electrical potential and is a component of the voltage drop across the cell pair.

**Figure 4.3: Electrodialysis pair schematic illustrating a) the electrolyte concentration profile, b) the potential gradient profile due to resistances, and c) the potential gradient profile due to concentration differences**



Ion transport in the Y direction occurs by advection. Ion concentrations in the diluate stream decrease in the Y direction from the inlet to the outlet of the cell pair, and those in the concentrate stream increase.

Figure 4.3a) illustrates concentration gradients across the cell pair. The points 1 through 9 in the figure mark concentration transition points that occur at membrane surfaces and boundary layers. Ions are transported at a faster rate through the membranes than through solution. The difference in transport rates leads to a depletion of ions at the membrane surface in the diluate and an accumulation at the membrane surface in the concentrate. Hence, concentrations in the diluate are higher in the bulk solution than in the boundary layers adjacent to the membranes. The opposite is true in the concentrate compartments. Ion concentrations are higher in the boundary layers than in the bulk solution. Ion concentrations are considerably higher in the membranes than in solution to balance membrane fixed charges, and these ions are almost exclusively counterions.

Figure 4.3b) shows voltage drop across the cell pair due to resistance. Voltage drop across a cell pair is determined by the following three components:

- Voltage necessary to overcome resistance in solution
- Voltage necessary to overcome resistance through the membrane, and
- Voltage required to counteract the electromotive force generated by chemical potential differences

Because resistance is inversely proportional to conductivity, voltage drops in solution are greatest in the diluate, particularly across boundary layers where ion concentrations are lowest. Voltage drops across membranes are proportional to area resistances of the membranes. Energy requirements are minimized by maintaining narrow spacing between membranes, selection of membranes with low resistance, and control of hydrodynamic conditions to minimize boundary layer thickness.

Potential gradients due to concentration differences are shown in Figure 4.2c. Differences in chemical potential exert an electromotive force that must be counteracted by the applied voltage difference to initiate ion flow.

The voltage drop across the cell pair is the sum of diffusion potentials and voltage drops due to resistances of the two solution compartments and the membranes.

The voltage drop due to a difference in chemical potentials between two solutions can be expressed as follows, where  $\Delta U$  is potential difference, the subscript  $a$  represents anion, and the subscript  $c$ , cation:

$$\Delta U_{1-2dp} = \frac{RT}{F} \int_1^2 (t_a^d - t_c^d) d(\ln a)$$

Therefore, the voltage drop across the cell pair due to chemical potential differences is as follows where the superscripts are  $d$  for diluate,  $c$  for concentrate,  $am$  for anion exchange membrane, and  $cm$  for cation exchange membrane:

$$\Delta U_{dp} = \frac{RT}{F} \left[ \begin{aligned} & \left( t_a^d - t_c^d \right) \int_1^2 d(\ln a) + \left( t_a^d - t_c^d \right) \int_3^4 d(\ln a) + \left( t_a^{am} - t_c^{am} \right) \int_4^5 d(\ln a) + \\ & \left( t_a^c - t_c^c \right) \int_5^6 d(\ln a) + \left( t_a^c - t_c^c \right) \int_7^8 d(\ln a) + \left( t_a^{cm} - t_c^{cm} \right) \int_8^9 d(\ln a) \end{aligned} \right]$$

This expression can be simplified by recognizing the following characteristics of ion transport in solution and through the membranes:

- Transport numbers of cations and anions in an electrolyte solution do not differ by very much (Strathman 2004). Assume  $t_a^d = t_c^d$  and  $t_a^c = t_c^c$ .
- Current through the membranes is carried almost exclusively by counterions. Assume  $t_a^{am} = 1$ ,  $t_c^{am} = 0$ ,  $t_a^{cm} = 0$ , and  $t_c^{cm} = 1$ .

Then,

$$\begin{aligned} \Delta U_{dp} &= \frac{RT}{F} \left[ \int_4^5 d(\ln a) - \int_8^9 d(\ln a) \right] \\ \Delta U_{dp} &= \frac{RT}{F} \left[ \ln \left( \frac{a_5}{a_4} \right) - \ln \left( \frac{a_9}{a_8} \right) \right] \end{aligned}$$

Replacing activities with activity coefficients and molar concentrations

$$\Delta U_{dp} = \frac{RT}{F} \left[ \ln \left( \frac{\gamma_5 C_5}{\gamma_4 C_4} \right) - \ln \left( \frac{\gamma_9 C_9}{\gamma_8 C_8} \right) \right]$$

The potential drop in solution from point 1 to point 2 due to resistance is as follows:

$$\begin{aligned} \Delta U_{1-2IR} &= i \int_1^2 \frac{dx}{C\Lambda} \\ C\Lambda &= k \\ \Delta U_{1-2IR} &= i \int_1^2 \frac{dx}{k} \end{aligned}$$

Potential drops through the anion and cation membranes are

$$\begin{aligned} \Delta U_{amIR} &= i r_{am} \\ \Delta U_{cmIR} &= i r_{cm} \end{aligned}$$



Summing terms across the cell pair, the potential drop due to resistance is

$$\Delta U_{IR} = i \left[ \int_1^2 \frac{dx}{C\Lambda} + \int_2^3 \frac{dx}{C\Lambda} + \int_3^4 \frac{dx}{C\Lambda} + r_{am} + \int_5^6 \frac{dx}{C\Lambda} + \int_6^7 \frac{dx}{C\Lambda} + \int_7^8 \frac{dx}{C\Lambda} + r_{cm} \right]$$

If it is assumed that concentration variation across each diluate and concentrate cell is negligible and recognizing that  $\Delta \gg \delta$ , the potential drop due to resistance can be simplified to

$$\Delta U_{IR} = i \left[ \frac{\Delta}{k_d} + r_{am} + \frac{\Delta}{k_c} + r_{cm} \right]$$

Combining diffusion potential and resistance terms, the total potential drop across the cell pair is

$$\Delta U = \Delta U_{dp} + \Delta U_{IR} = \frac{RT}{F} \left[ \ln \left( \frac{\gamma_c C_c}{\gamma_d C_d} \right) - \ln \left( \frac{\gamma_d C_d}{\gamma_c C_c} \right) \right] + i \left[ \frac{\Delta}{k_d} + r_{am} + \frac{\Delta}{k_c} + r_{cm} \right]$$

If ratios of diluate and concentrate activities are replaced with the ratios of their conductivities, the equation simplifies to

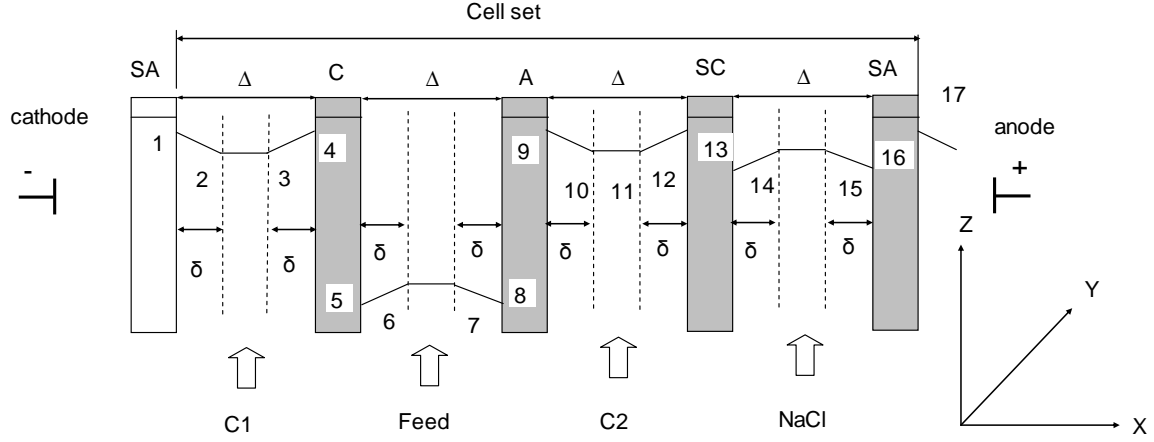
$$\Delta U = \frac{RT}{F} \left[ \ln \left( \frac{k_c}{k_d} \right) - \ln \left( \frac{k_d}{k_c} \right) \right] + i \left[ \frac{\Delta}{k_d} + r_{am} + \frac{\Delta}{k_c} + r_{cm} \right]$$

The electrodialysis metathesis (EDM) cell set is illustrated schematically in Figure 4.4. The EDM cell set comprises from left to right: concentrate compartment 1, cation selective membrane C, diluate compartment, anion selective membrane A, concentrate compartment 2, monovalent cation selective membrane SC, NaCl compartment, and monovalent anion selective membrane SA. All flows are co-current in the Y direction, and the electrodes create an electrical potential gradient in X direction. The concentration profile is shown.

Voltage drops in the EDM cell set are analogous to the basic ED cell pair except the additional concentrate compartment, the NaCl compartment, and the two additional membranes must be accounted for. The equation for voltage drop across the EDM cell set is developed with assumptions used to develop the ED equation:

- Concentration variations within each compartment have negligible effect on voltage drop.
- Cation and anion transport numbers in a solution are similar.
- Current is carried in membranes exclusively by counterions.

**Figure 4.4: Electrodialysis metathesis cell set illustrating the electrolyte concentration profile**



With application of the above assumptions, the voltage drop due to diffusion potential in the EDM cell set is

$$\Delta U_{dp} = \frac{RT}{F} \left[ - \int_4^5 d(\ln \gamma C) + \int_8^9 d(\ln \gamma C) - \int_{12}^{13} d(\ln \gamma C) + \int_{16}^{17} d(\ln \gamma C) \right]$$

$$\Delta U_{dp} = \frac{RT}{F} \left[ - \ln \left( \frac{\gamma_d C_d}{\gamma_{c1} C_{c1}} \right) + \ln \left( \frac{\gamma_{c2} C_{c2}}{\gamma_d C_d} \right) - \ln \left( \frac{\gamma_{NaCl} C_{NaCl}}{\gamma_{c2} C_{c2}} \right) + \ln \left( \frac{\gamma_{c1} C_{c1}}{\gamma_{NaCl} C_{NaCl}} \right) \right]$$

If activity ratios are replaced with conductivity ratios,

$$\Delta U_{dp} = \frac{RT}{F} \left[ - \ln \left( \frac{k_d}{k_{c1}} \right) + \ln \left( \frac{k_{c2}}{k_d} \right) - \ln \left( \frac{k_{NaCl}}{k_{c2}} \right) + \ln \left( \frac{k_{c1}}{k_{NaCl}} \right) \right]$$

With the assumption that concentration variations across each compartment are negligible and recognizing that  $\Delta \gg \delta$ , the potential drop due to resistance in the EDM cell set is

$$\Delta U_{IR} = i \left[ \frac{\Delta}{k_{c1}} + r^{cm} + \frac{\Delta}{k_d} + r^{am} + \frac{\Delta}{k_{c2}} + r^{scm} + \frac{\Delta}{k_{NaCl}} + r^{sam} \right]$$

Combining diffusion potential and resistance terms,

$$\Delta U = \Delta U_{dp} + \Delta U_{IR} = \frac{RT}{F} \left[ -\ln\left(\frac{k_d}{k_{c1}}\right) + \ln\left(\frac{k_{c2}}{k_d}\right) - \ln\left(\frac{k_{NaCl}}{k_{c2}}\right) + \ln\left(\frac{k_{c1}}{k_{NaCl}}\right) \right] + i \left[ \frac{\Delta}{k_{c1}} + r_{cm} + \frac{\Delta}{k_d} + r_{am} + \frac{\Delta}{k_{c2}} + r_{scm} + \frac{\Delta}{k_{NaCl}} + r_{sam} \right]$$

A shadow factor,  $\beta$ , is applied to the terms containing current density to account for the membrane area blocked by the spacer. The final equation for potential drop is then

$$\Delta U = \Delta U_{dp} + \Delta U_{IR} = \frac{RT}{F} \left[ -\ln\left(\frac{k_d}{k_{c1}}\right) + \ln\left(\frac{k_{c2}}{k_d}\right) - \ln\left(\frac{k_{NaCl}}{k_{c2}}\right) + \ln\left(\frac{k_{c1}}{k_{NaCl}}\right) \right] + i\beta \left[ \frac{\Delta}{k_{c1}} + r_{cm} + \frac{\Delta}{k_d} + r_{am} + \frac{\Delta}{k_{c2}} + r_{scm} + \frac{\Delta}{k_{NaCl}} + r_{sam} \right]$$

Variables used in the model are listed in Table 4.1. The same basic EDM stack was used for evaluation of each of the sites. Therefore, variable values were the same for each of the three sites with the exception of the first two, RO concentrate normality and RO concentrate flow. These values are site specific and changed at each treatment facility.

The EDM stack is unchanged from site to site, and therefore membrane size and area resistance is the same for each site. The limiting polarization parameter exponent and coefficient were determined in Experiment 2 and are properties of the stack. Conductivities in the two concentrate solutions, the sodium chloride solution, and the electrode rinse solution are all operator-controlled variables through the addition of dilution water to the concentrate streams and salt solution to the sodium chloride and electrode rinse solutions. Conductivity limits were set at 50 mS/cm in the mixed sodium concentrate and 150 mS/cm in the mixed chloride concentrate to avoid membrane scaling. Conductivity was set at 50 mS/cm for the sodium chloride and electrode rinse compartments. A water temperature of 26 °C was used.

The redundancy factor was used to account for stacks being out of service for cleaning. During testing, the membranes became scaled and did not respond to a CIP. It was necessary to take the stack apart and clean the membranes manually. The redundancy factor was multiplied by the number of stacks required by capacity to determine the design stack number. For example, if 10 stacks were required for capacity, with a redundancy factor of 1.4, the number of stacks for design would be 14. Based on the level of effort required for the manual cleaning process, the research team used a redundancy factor of 1.4. The design stack number was used to calculate construction cost. The number of stacks required for capacity was used to calculate energy and NaCl consumption costs.

The last four rows in the table contain cost variables. The total cost to apply EDM treatment of concentrate at any treatment plant will depend on many site-specific conditions, for example, the need for a new building or site improvements. To make this a cost template that can be used for any water treatment plant site, we did not include site-specific variables in the cost projections. Rather, the total treatment costs presented here comprise the three main components of EDM treatment cost: EDM construction cost, EDM electricity cost, and NaCl consumption cost. We set the EDM unit installed cost at \$100,000 per stack based on information from Veolia, one of the potential manufacturers. We used an electricity unit cost of \$0.12 per kWh. We calculated present worth values with a term of 20 years and a rate of 0.04.

**Table 4.1: Variables used to calculate EDM power and cost**

Variable	Value
RO concentrate normality (meq/L)	32.6
RO concentrate flow (gpm)	300
EDM membrane spacer width (cm)	0.08
EDM membrane width (cm)	40
EDM membrane length (cm)	160
EDM membrane effective area (cm <sup>2</sup> )	4083
EDM number of quads	120
Limiting PP coefficient ( $A \text{ cm eq}^{-1} \text{ s}^{0.54} \text{ cm}^{-0.54}$ )	206
Limiting polarization parameter exponent	0.54
EDM cation exchange membrane area resistance ( $\Omega \text{ cm}^2$ )	7.5
EDM anion exchange membrane area resistance ( $\Omega \text{ cm}^2$ )	8.0
Limit for mixed sodium concentrate conductivity (mS/cm)	50
Limit for mixed sodium concentrate conductivity (mS/cm)	150
Sodium chloride solution conductivity (mS/cm)	50
Electrode solution conductivity (mS/cm)	50
EDM feed water temperature (°C)	26
EDM stack redundancy factor	1.4
EDM construction cost per stack	\$100,000
Electricity unit cost (\$/kWh)	\$0.12
Present worth term (years)	20
Present worth rate	0.04

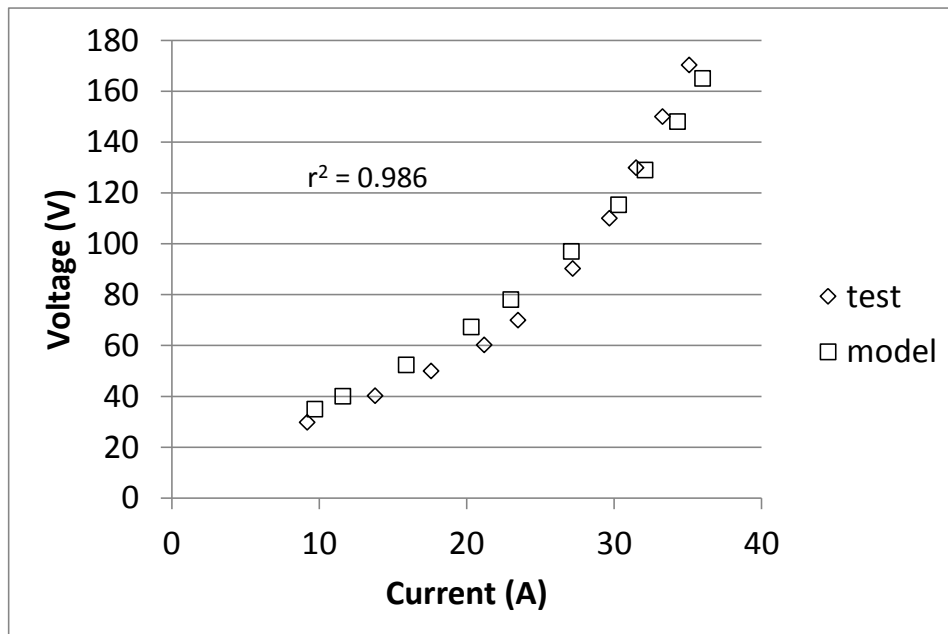
EDM treatment was evaluated at the three sites by setting a treatment goal for EDM conductivity specific to the water quality requirements at each site. The EDM diluate water quality goal was used to calculate the voltage and current required for treatment. The capacity of each EDM stack was calculated with the selected feed cell velocity. The number of stacks required was calculated with the total concentrate flow and EDM stack capacity. Water quality and current were used to calculate the polarization parameter, and the limiting polarization parameter was calculated using the coefficient and exponent determined in Experiment 2. We used 80 percent of the limiting polarization parameter as the maximum allowable value for safe operation.

#### 4.1.2 Model calibration

The model was calibrated using data from Experiment 2, and the result is shown in Figure 4.5. The graph shows test data recorded during Experiment 2 plotted with voltage and current values calculated with the model. To calibrate the model, we adjusted two variables: the shadow factor,  $\beta$ , and current utilization,  $\xi$ . The model values were calculated with a shadow factor of 1.65 and a current utilization of 0.65. The square of the correlation coefficient,  $r^2$ , was calculated with the sum of squared deviations from the regression line,  $SS_{res}$ , and the sum of squared deviations from the mean,  $SS_{tot}$ . The model fit the test data with an  $r^2$  value of 0.986, showing a close correlation of the model to field results.

$$r^2 = 1 - \frac{SS_{res}}{SS_{tot}}$$

**Figure 4.5: Data from Experiment 2 plotted with EDM model calculations**



With the model calibrated, the next step was calculation of energy and cost to treat RO concentrate at each of the three treatment plants. This calculation was performed for each site and is described in the following sections.

## 4.2 Beverly Hills Water Treatment Facility

### 4.2.1 Plant Description

BHWTF treats groundwater with RO membranes and packed tower aeration. Ground water is prefiltered and dosed with acid and antiscalant ahead of the RO membrane skids. The RO membranes are typically operated at 74 percent recovery to produce 1,150 gpm of permeate and 300 gpm of concentrate. Typical TDS concentrations are 750 mg/L in the feed, 150 mg/L in the permeate, and 3,200 mg/L in the concentrate. Permeate is treated with packed tower aeration to remove hydrogen sulfide, and the stripped hydrogen sulfide is treated with air phase GAC. RO concentrate is discharged to the sewer.

### 4.2.2 Concentrate Treatment Objective

In the treatment approach evaluated for the BHWTF, EDM diluate would be blended with RO permeate to produce final product water. Hence, the treatment goal was to produce diluate that, when blended with RO permeate, achieves finished water goals. The criterion used for finished water quality was a TDS of 400 mg/L or less or a conductivity of 670  $\mu\text{S}/\text{cm}$  or less. The BHWTF RO system typically produced permeate with conductivity around 260  $\mu\text{S}/\text{cm}$ . Therefore the treatment goal for EDM diluate was a conductivity of 1800  $\mu\text{S}/\text{cm}$  or less.

### 4.2.3 Calculation of Cost and Energy Requirements

Input data used in the Beverly Hills calculations are shown in Table 4.2. The RO concentrate normality was calculated from laboratory analyses of RO concentrate during testing. The calculation was performed with an RO flow of 300 gpm, a typical value for the plant.

**Table 4.2: Variables used to evaluate treatment at the BHWTF**

Variable	Value
RO concentrate normality (meq/L)	32.6
RO concentrate flow (gpm)	300

The research team optimized the EDM design for the BHWTF by evaluating the sensitivity of treatment cost to the two key factors: mode of EDM operation and cell velocity. The following three modes of EDM operation were evaluated:

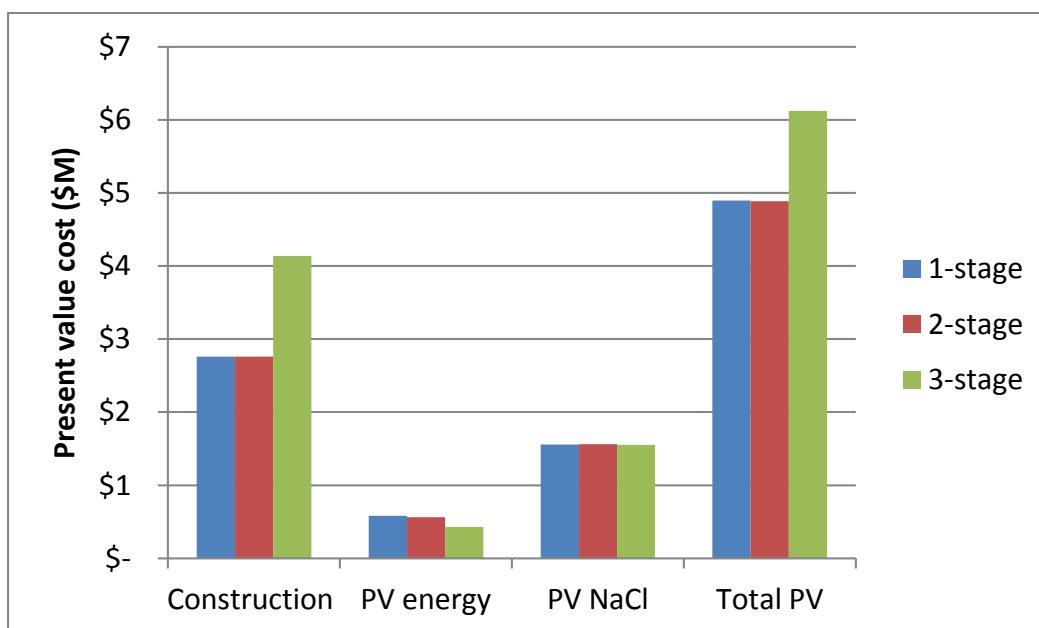
- One-stage treatment with recirculation of EDM diluate as needed
- Two-stage treatment with no recirculation of EDM diluate
- Three-stage treatment with no recirculation of EDM diluate

The number of stages refers to the number of EDM stages in series. With recirculation of EDM diluate to the feed, the influent is diluted, and consequently the energy required for each stack

at the diluate treatment goal is less than it would be without recirculation. More EDM stacks are required in parallel, however, because the influent flow comprises both the RO concentrate flow and the recirculated EDM diluate.

The results of the effect of mode of operation on treatment cost for the BHWTF are shown in Figure 4.6. We used a cell velocity of 5 cm/s for this evaluation. A recirculation ratio of 1.0 was required to meet the treatment goal with one EDM stage. Operating one stage with a recirculation ratio of one requires the same number of stacks as operating two stages without recirculation. Hence construction cost was the same for the two options. The NaCl consumed depends only on the treatment goal because the same number of total equivalents is removed from the RO concentrate regardless of the number of EDM stages used. Therefore, the NaCl cost was the same for all three modes of operation, and energy and construction cost were the only cost differentiators. There was no significant difference in energy cost between one-stage and two-stage operation. Consequently, the treatment cost for one-stage and two-stage operation were the same. The energy cost for three-stage operation was slightly less than the other two options, but the construction cost was significantly greater. Therefore the total cost for three-stage operation was greater than for either of the other two options, costs of which were essentially equal. The research team decided to evaluate the BHWTF with one-stage EDM treatment. In practice, it would seem logical to plumb the stacks to allow operation in series or in parallel.

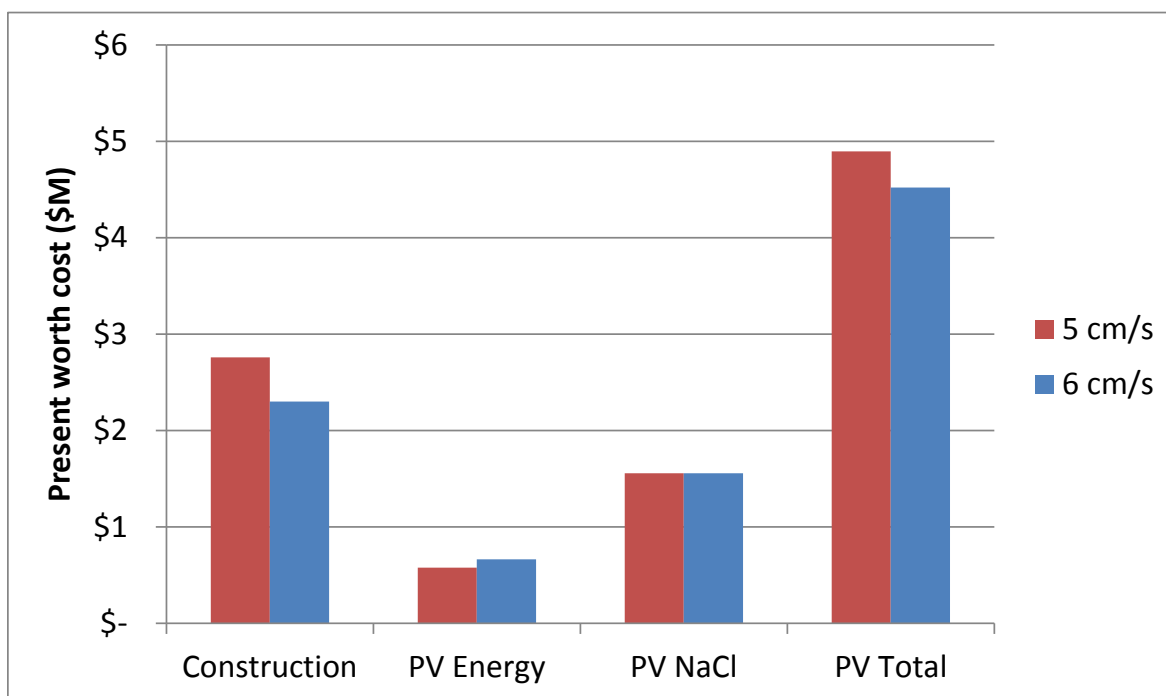
**Figure 4.6: Effect of EDM mode of operation on present value cost in EDM model calculations for BHWTF**



The results of the evaluation of cell velocity are shown in Figure 4.7. Cell velocity is an important operational variable. As cell velocity increases, the number of stacks required decreases, but the energy required by each stack increases. Three EDM diluate cell velocities

were evaluated: 5 cm/s, 6 cm/s, and 7 cm/s. The polarization parameter exceeded 80 percent of the limiting value at a cell velocity of 7 cm/s, and therefore costs were not reported for that velocity. Present value costs are shown for construction, energy, NaCl, and their total. The ratio of polarization parameter to limiting polarization parameter,  $PP/PP_{lim}$ , was 0.71 at 5 cm/s and 0.78 at 6 cm/s. The total cost appears to be slightly lower at a cell velocity of 6 cm/s, but the research team decided to conduct the evaluation with a cell velocity of 5 cm/s to provide a greater safety factor with respect to the limiting polarization parameter.

**Figure 4.7: Effect of EDM diluate cell velocity on present value cost in EDM model calculations for BHWTF**



Results of the evaluation of EDM treatment of the BHWTF RO concentrate are shown in Table 4.3. The final EDM diluate conductivity was 1.6 mS/cm, which was safely below the treatment goal. Twenty parallel stacks were required to treat the 300 gpm RO concentrate flow with a recycle ratio of 1.0. The current was 22.3 A, and the stack voltage was 92 V. The power required was 2.0 kW for each stack, and the EDM energy consumption was 0.60 kWh/m<sup>3</sup>.

The polarization parameter was 60 percent of the limiting polarization parameter. The total NaCl consumption was 1,900 kilograms per day (kg/d). EDM recovery, accounting for the dilution water added to the two concentrate streams, was 95 percent. The total system recovery comprising water recovered by the BHWTF RO membranes and RO concentrate recovered by the EDM stacks was 98 percent.



**Table 4.3: Water quality and energy results of the BHWTF evaluation**

Item	Units	Value
Cell velocity	(cm/s)	5.0
Feed normality	(meq/L)	22.8
Diluate normality	(meq/L)	13.0
Feed conductivity	(mS/cm)	2.9
Diluate conductivity	(mS/cm)	1.6
Mixed sodium concentrate conductivity	(mS/cm)	50
Mixed chloride conductivity	(mS/cm)	150
Sodium chloride conductivity	(mS/cm)	50
Electrode rinse conductivity	(mS/cm)	50
Number of stacks for flow	-----	20
Design number of stacks	-----	28
Recycle ratio	-----	1.0
Flow per stack	(gpm)	30
Current per stack	(A)	22.3
Voltage per stack	(V)	92
Power per stack	(kW)	2.0
Energy consumption	(kWh/m <sup>3</sup> )	0.60
Polarization parameter	(A cm/eq)	313
Limiting polarization parameter	(A cm/eq)	441
NaCl consumption all stacks	(kg/d)	1900
Concentrate recovery <sup>1</sup>	-----	0.95
Total system recovery <sup>2</sup>	-----	0.99
1. EDM system recovery accounting for dilution water and NaCl makeup water. 2. Total recovery is the combined recoveries of the RO and EDM systems.		

Cost results of the evaluation are presented in Table 4.4. The EDM construction cost for 28 stacks was \$2,800,000. The annual operating costs were \$43,000 for EDM electricity and \$115,000 for NaCl. The total present value cost was \$4,936,000. The unit treatment cost, comprising amortized capital cost and operating cost for electricity and NaCl was \$2.28 per thousand gallons of concentrate recovered or \$744 per acre-foot.

**Table 4.4: Cost results of the BHWTF evaluation**

Item	Units	Cost
EDM construction cost all stacks	(\$)	\$2,800,000
EDM electricity cost	(\$/yr)	\$43,000
EDM NaCl cost	(\$/yr)	\$115,000
Present value electricity cost	(\$)	\$580,000
Present value NaCl cost	(\$)	\$1,556,000
Total present value cost	(\$)	\$4,936,000
Concentrate treatment cost	(\$/kgal)	\$2.28
Concentrate treatment cost	(\$/ac-ft)	\$744

## **4.3 Santa Rosa Water Reclamation Facility**

### **4.3.1 Plant Description**

The evaluation for RCWD was for treatment of RO brine from SRWRF for reuse. Water quality data used for the evaluation of EDM treatment of RO concentrate at SRWRF are shown in Table 4.5. The raw water data are measurements of the SRWRF tertiary treated wastewater effluent. We used the raw water data with RO membrane design software (Hydronics Membrane Solutions Design Software, v. 2012) to project RO concentrate and permeate ion concentrations. The evaluation was conducted with RO membranes predicted to achieve 96 percent rejection of TDS and at an RO recovery of 85 percent.

**Table 4.5: Water quality data for the SRWRF evaluation**

Ion	Units	Raw water	RO permeate	RO concentrate
Ca	mg/L	53	0.51	350
Mg	mg/L	18	0.17	119
Na	mg/L	145	6.63	932
K	mg/L	14	0.80	89
NH <sub>4</sub>	mg/L	0.4	0.023	2.5
Ba	mg/L	0.04	0.00	0.3
Sr	mg/L	0.39	0.00	2.6
HCO <sub>3</sub>	mg/L	147	6.68	942
SO <sub>4</sub>	mg/L	127	0.82	842
Cl	mg/L	186	4.75	1213
F	mg/L	0.6	0.03	3.8
NO <sub>3</sub>	mg/L	31	5.45	176
B	mg/L	0.49	0.49	0.49
SiO <sub>2</sub>	mg/L	18	0.44	142
TDS	mg/L	741	27	4791
pH	S.U.	7.0	5.7	7.88
Conductivity	mS/cm	1.10	0.04 <sup>1</sup>	5.99 <sup>2</sup>
Normality	(meq/L)	11	0.35	54
Notes:				
1. Permeate conductivity calculated as 0.67 x TDS/1000				
2. Concentrate conductivity calculated as 0.80 x TDS/1000				

#### 4.3.2 Concentrate Treatment Objective

The treatment objective for EDM in this desktop study was to produce diluate with the same TDS as the RO feed. It must be noted, however, that uncharged contaminants such as silica are not removed by EDM, and therefore concentrations of these neutral charge contaminants would exist in the EDM diluate at the same level as in the RO concentrate. Depending on the contaminant, the intended reuse of the water, and regulations governing reuse and the contaminant, EDM treated concentrate at water reclamation facilities may need to be blended with the RO feed so that the water is treated by RO before it is reused. If this is the case, some treatment of the EDM diluate would be necessary to prevent accumulation of silica and other uncharged contaminants in the RO feed. More detailed study at such sites would be required to identify any site specific contaminants of concern that would require additional treatment.

### 4.3.3 Calculation of Costs and Energy Requirements

Input data used in the SRWRF calculations are shown in Table 4.6. The RO concentrate normality was calculated from ion concentrations in Table 4.6. We calculated RO concentrate flow based on an RO influent flow of 3,645 gpm and 85 percent RO recovery.

**Table 4.6: Variables used for the SRWRF evaluation**

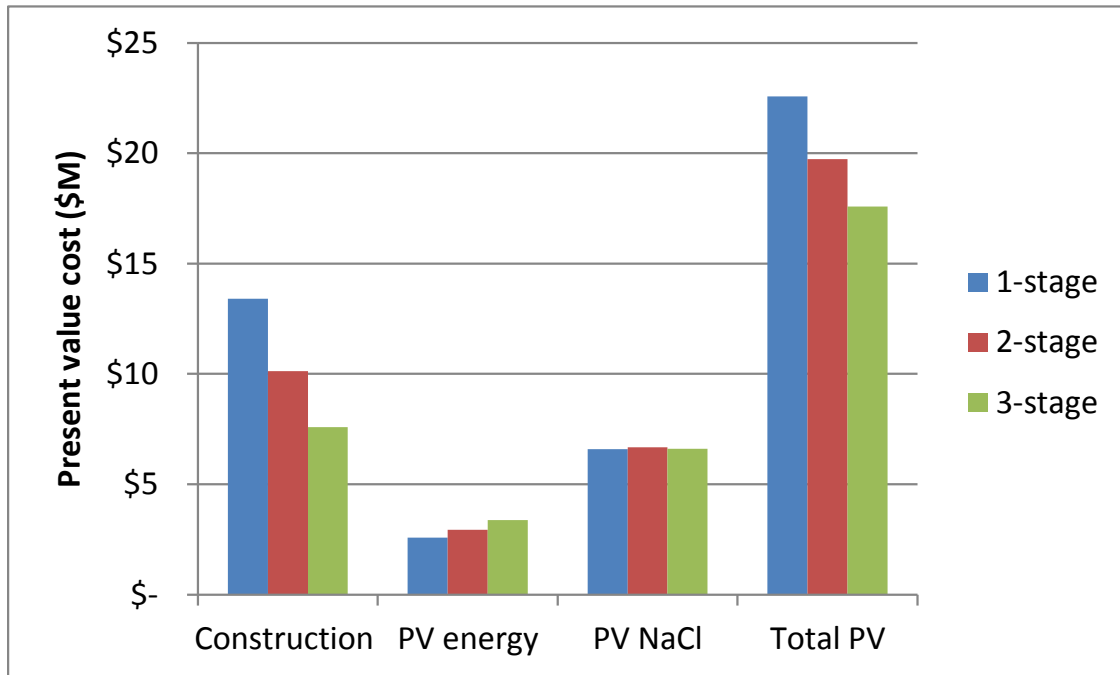
Variable	Value
RO concentrate normality (meq/L)	56
RO concentrate flow (gpm)	550

As with the Beverly Hills evaluation, the research team evaluated the sensitivity of treatment cost to mode of EDM operation and cell velocity. The following three modes of EDM operation were evaluated:

- One-stage treatment with recirculation of EDM diluate as needed
- Two-stage treatment with recirculation of EDM diluate
- Three-stage treatment with no recirculation of EDM diluate

The results of the effect of mode of operation on treatment cost for the SRWRF are shown in Figure 4.8. We used a cell velocity of 5 centimeters per second (cm/s) for this evaluation. At a recirculation ratio of 4.3 with EDM stage, the total present value cost was calculated to be \$22.6 Million. For a recirculation ratio of 1.0 to meet the treatment goal with two EDM stages (diluate of the second stack in the series is recirculated to the influent of the first stack), the total present value cost was calculated to be \$19.7 Million. When no recirculation was required to meet the treatment goal with three EDM stages, the total present value cost was \$17.6 M.

**Figure 4.8: Effect of EDM mode of operation on present value cost in EDM model calculations for SRWRF**

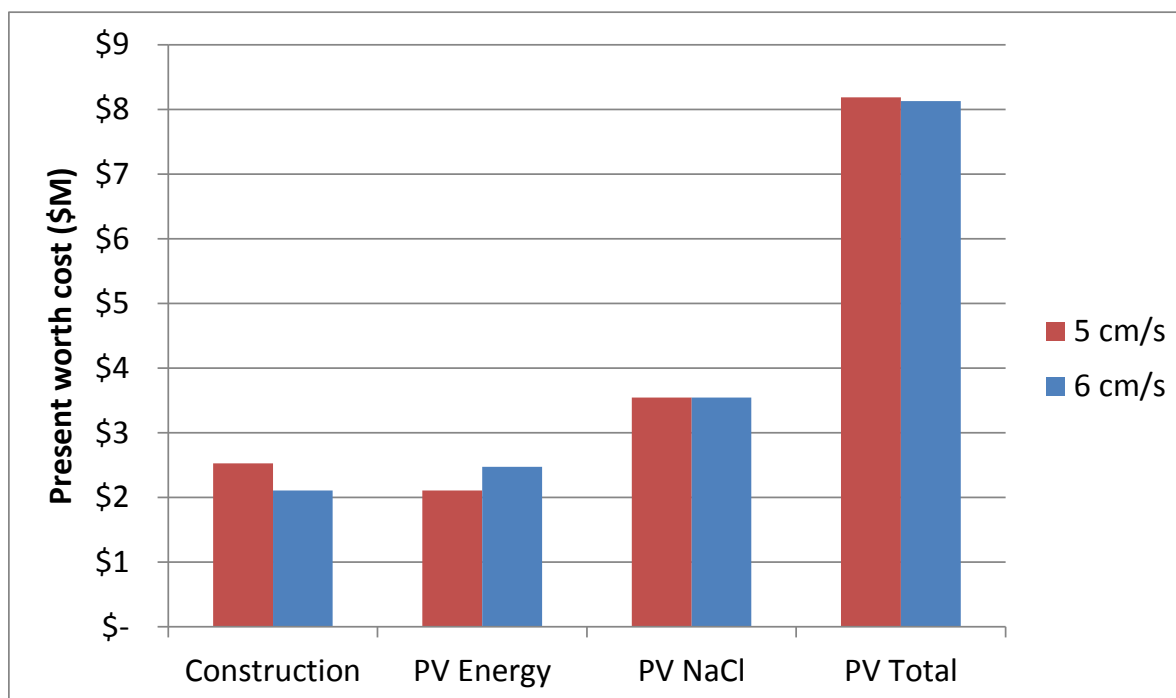


$PP/PP_{lim}$ , was 0.75 for one-stage or two-stage operation and 0.71 for three-stage operation. Operation with three EDM stages had the lowest calculated present value cost. Operation with two stages was 11 percent more expensive, and operation with one stage was 26 percent more expensive. The research team selected a three-stage operation for the evaluation.

The results of the evaluation of cell velocity are shown in Figure 4.9. Four EDM diluate cell velocities were evaluated: 5 cm/s, 6 cm/s, 7 cm/s, and 8 cm/s for three stage EDM treatment. The guideline for polarization parameter, 80 percent of limiting polarization parameter, was exceeded at cell velocities of 7 cm/s and 8 cm/s, and consequently costs are not shown for these two higher velocities. Present value costs are shown for construction, energy, NaCl, and their total.

Construction costs were lower at 6 cm/s than at 5 cm/s, but energy costs were higher. The total present value cost was lower at the higher velocity.  $PP/PP_{lim}$ , was 0.78 at 6 cm/s compared with 0.70 at a cell velocity of 5 cm/s. The research team decided to conduct the evaluation with a cell velocity of 5 cm/s to provide a more conservative safety factor with respect to the limiting polarization parameter.

**Figure 4.9: Effect of EDM diluate cell velocity on present value cost in EDM model calculations for SRWRF**



Results of the evaluation of EDM treatment of the SRWRF RO concentrate are shown in Table 4.7. The final EDM diluate conductivity (Stage 3) was 1.1 mS/cm. Eighteen parallel stacks in each stage were required to treat the 550 gpm RO concentrate flow. Stage 1 current was 47 A, and Stage 1 voltage was 129 V. Stage 2 current was 26 A, and Stage 2 voltage was 97 V. Stage 3 current was 15 A, and Stage 3 voltage was 81 V. The power required was 6.0 kilowatts (kW) for each Stage 1 stack, 2.6 kW for each Stage 2 stack, and 1.2 kW for each Stage 3 stack. The total energy consumption was 1.5 kilowatt hours per cubic meter (kWh/m<sup>3</sup>).

The polarization parameter was 71 percent of the limiting polarization parameter in Stage 1, 70 percent in Stage 2, and 69 percent in Stage 3. The total NaCl consumption was 6,891 kg/d. EDM recovery, accounting for the dilution water added to the two concentrate streams, was 93 percent in Stage 1, 96 percent in Stage 2, 99 percent in Stage 3, and 88 percent total. The total system recovery comprising water recovered by the SRWRF RO membranes and RO concentrate recovered by the EDM stacks was 98 percent.

**Table 4.7: Water quality and energy results of the SRWRF evaluation**

Item	Units	Stage 1	Stage 2	Stage 3	Total
Feed normality	(meq/L)	55.9	31.8	18.0	
Diluate normality	(meq/L)	31.8	18.0	10.0	
Feed conductivity	(mS/cm)	6.0	3.4	1.9	
Diluate conductivity	(mS/cm)	3.4	1.9	1.1	1.1
Mixed sodium concentrate conductivity	(mS/cm)	50	50	50	
Mixed chloride concentrate conductivity	(mS/cm)	150	150	150	
Sodium chloride conductivity	(mS/cm)	50	50	50	
Electrode rinse conductivity	(mS/cm)	50	50	50	
Number of stacks for flow	-----	18	18	18	54
Design number of stacks	-----	25	25	25	75
Flow per stack	(gpm)	31	31	31	550
Current per stack	(A)	54.5	30.5	17.2	
Voltage per stack	(V)	147	109	90	
Power per stack	(kW)	8.0	3.3	1.6	
Energy consumption	(kWh/m <sup>3</sup> )	1.5	0.5	0.2	2.2
Polarization parameter	(A cm/eq)	313	246	147	
Limiting polarization parameter	(A cm/eq)	441	441	441	
NaCl consumption all stacks	(kg/d)	4315	2363	1346	8024
EDM recovery <sup>1</sup>					0.89
Total system recovery <sup>2</sup>					0.97
Notes:					
1. Accounts for dilution water used to maintain EDM concentrate conductivities below the prescribed limits. 2. Total system recovery is the combined recovery of the SRWRF RO membranes and the recovery of RO concentrate by EDM.					

Cost results of the evaluation are presented in Table 4.8. The EDM construction cost for 54 stacks was \$5,400,000. The annual operating costs were \$189,000 for EDM electricity and \$509,000 for NaCl. The total present value cost was \$14,876,000. The unit treatment cost, comprising amortized capital cost and operating cost for electricity and NaCl, was \$4.48 per thousand gallons of concentrate recovered or \$1458 per acre-foot.

**Table 4.8: Cost results of the SRWRF evaluation**

Item	Units	Cost
EDM construction cost all stacks	(\$)	\$7,500,000
EDM electricity cost	(\$/yr)	\$249,000
EDM NaCl cost	(\$/yr)	\$486,000
Present value electricity cost	(\$)	\$3,383,000
Present value NaCl cost	(\$)	\$6,610,000
Total present value cost	(\$)	\$17,493,000
Concentrate treatment cost	(\$/kgal)	\$4.48
Concentrate treatment cost	(\$/ac-ft)	\$1458

## **4.4 Arcadia Water Treatment Plant**

### **4.4.1 Plant Description**

Santa Monica treats groundwater with RO for potable use at the Arcadia Water Treatment Plant (AWTP). Water quality data used for the evaluation of EDM treatment of RO concentrate at AWTP are shown in Table 4.9. The raw water data are averages of three measurements of the AWTP RO feed and RO concentrate from samples collected on April 8, April 15, and April 22 of 2014.



**Table 4.9: Water quality data for the AWTP evaluation**

Ion	Units	Raw water	RO concentrate
Ca	mg/L	113	637
Mg	mg/L	47	245
Na	mg/L	83	440
K	mg/L	3	17
Ba	mg/L	0.06	0.31
Sr	mg/L	0.7	3.6
HCO <sub>3</sub>	mg/L	363	1967
SO <sub>4</sub>	mg/L	247	1367
Cl	mg/L	110	570
SiO <sub>2</sub>	mg/L	34	170
TDS	mg/L	817	4333
pH	S.U.	7.58	7.83
Conductivity	mS/cm	1.23	5.53
Normality	(meq/L)	14	75

#### 4.4.2 Concentrate Treatment Objective

The treatment goal for EDM was to produce diluate that, when blended with the permeate from AWTP RO membranes, would produce a final product water with a TDS concentration of 400 mg/L or less. TDS of the RO permeate was 50 mg/L. Consequently, the treatment goal for EDM diluate was a TDS concentration of 2,380 mg/L or less or a conductivity of 2.9 mS/cm or less.

#### 4.4.3 Calculation of Costs and Energy Requirements

Input data used in the AWTP calculations are shown in Table 4.10. The RO concentrate normality was calculated from ion concentrations in Table 4.7. RO concentrate flow was based on current plant operating data.

**Table 4.10: Variable used for the AWTP evaluation**

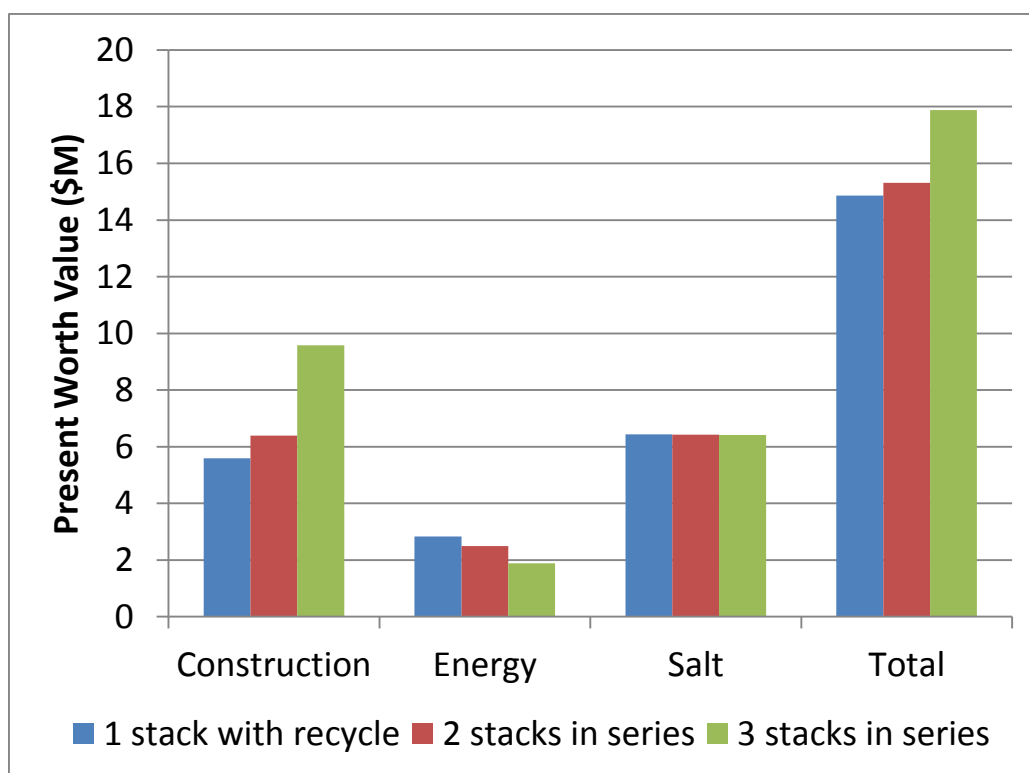
Variable	Value
RO concentrate normality (meq/L)	48
RO concentrate flow (gpm)	972

As before, the research team evaluated the sensitivity of treatment cost to mode of EDM operation and cell velocity. The following three modes of EDM operation were evaluated:

- One-stage treatment with recirculation of EDM diluate as needed.
- Two-stage treatment with no recirculation of EDM diluate.
- Three-stage treatment with no recirculation of EDM diluate.

The results of the effect of mode of operation on treatment cost for the SRWRF are shown in Figure 4.10. We used a cell velocity of 5 cm/s for this evaluation. One-stage EDM operation met the treatment goal with a recycle ratio of 0.75. No recycle was required for the two and three stage options. Construction cost was least for one stage EDM operation and greatest for three stage EDM operation. Conversely, energy costs were greatest for one stage EDM operation and least for three stage EDM operation. Total treatment cost was least for one stage EDM operation. In this case, the polarization parameter for one stage EDM was only 65 percent of the limiting polarization parameter. The research team decided to use one stage operation for the evaluation of the AWTP.

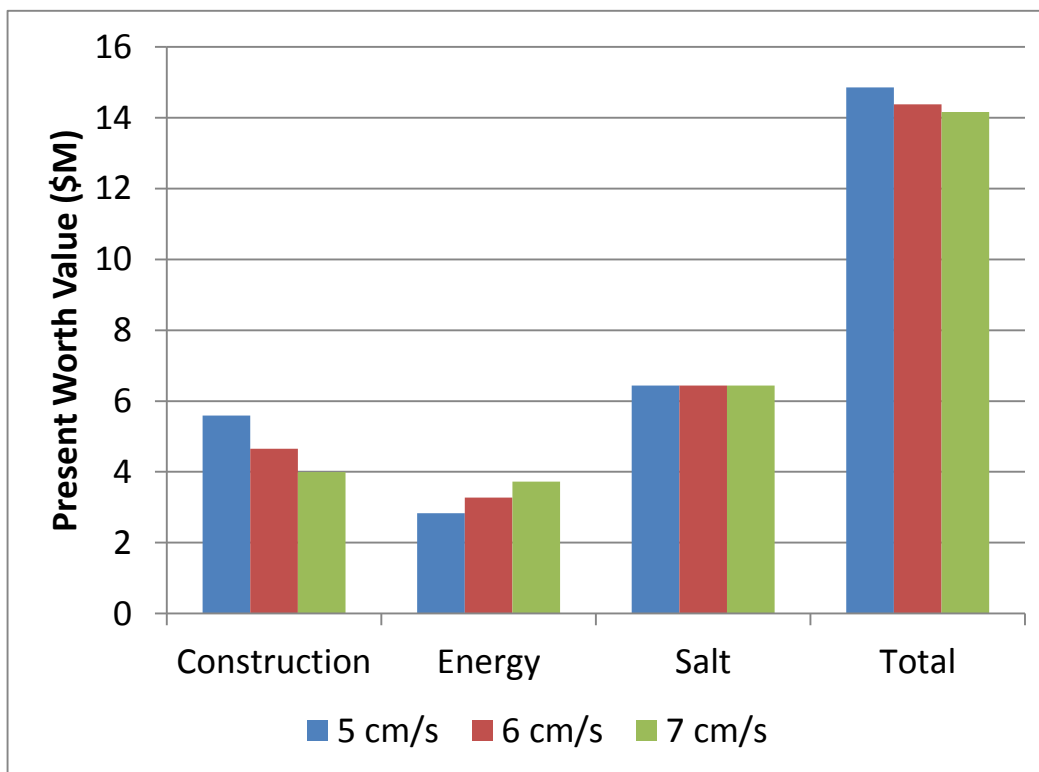
**Figure 4.10: Effect of EDM mode of operation on present value cost in EDM model calculations for AWTP**



The effects of cell velocity on treatment cost in the AWTP evaluation are shown in Figure 4,11, The ratio of polarization parameter to limiting polarization parameter was 0.65 at 5 cm/s, 0.72 at 6 cm/s, and 0.78 at 7 cm/s. Costs were not calculated for a velocity of 8 cm/s because the

polarization parameter was too high. Construction cost decreased as cell velocity increased, but energy cost increased as cell velocity increased. The total present value cost was greatest at a cell velocity of 5 cm/s and least at a cell velocity of 7 cm/s. The research team decided to conduct the evaluation with a cell velocity of 5 cm/s to provide a greater safety factor with the polarization parameter.

**Figure 4.11: Effect of EDM cell velocity on present value cost in EDM model calculations for AWTP**



Results of the evaluation of EDM treatment of the AWTP RO concentrate are shown in Table 4.11. The final EDM diluate conductivity (Stage 3) was 1.1 mS/cm. Eighteen parallel stacks in each stage were required to treat the 550 gpm RO concentrate flow. Stage 1 current was 47 A, and Stage 1 voltage was 129 V. Stage 2 current was 26 A, and Stage 2 voltage was 97 V. Stage 3 current was 15 A, and Stage 3 voltage was 81 V. The power required was 6.0 kW for each Stage 1 stack, 2.6 kW for each Stage 2 stack, and 1.2 kW for each Stage 3 stack. The total energy consumption was 1.5 kWh/m<sup>3</sup>.

The polarization parameter was 71 percent of the limiting polarization parameter in Stage 1, 70 percent in Stage 2, and 69 percent in Stage 3. The total NaCl consumption was 6,891 kg/d. EDM recovery, accounting for the dilution water added to the two concentrate streams, was 93 percent in Stage 1, 96 percent in Stage 2, 99 percent in Stage 3, and 88 percent total. The total system recovery comprising water recovered by the SRWRF RO membranes and RO concentrate recovered by the EDM stacks was 98 percent.

**Table 4.11: Water quality and energy results of the AWTP evaluation**

Item	Units	Stage 1
Feed normality	(meq/L)	34.5
Diluate normality	(meq/L)	19.0
Feed conductivity	(mS/cm)	4.1
Diluate conductivity	(mS/cm)	2.6
Mixed sodium concentrate conductivity	(mS/cm)	50
Mixed chloride concentrate conductivity	(mS/cm)	150
Sodium chloride conductivity	(mS/cm)	50
Electrode rinse conductivity	(mS/cm)	50
Number of stacks for flow	-----	56
Design number of stacks	-----	78
Flow per stack	(gpm)	31
Current per stack	(A)	33
Voltage per stack	(V)	115
Power per stack	(kW)	4.1
Energy consumption	(kWh/m <sup>3</sup> )	0.8
Polarization parameter	(A cm/eq)	332
Limiting polarization parameter	(A cm/eq)	441
NaCl consumption all stacks	(kg/d)	8548
EDM recovery <sup>1</sup>		0.93
Total system recovery <sup>2</sup>		0.99
Notes:		
1. Accounts for dilution water used to maintain EDM concentrate conductivities below the prescribed limits. 2. Total system recovery is the combined recovery of the SRWRF RO membranes and the recovery of RO concentrate by EDM.		

Cost results of the AWTP evaluation are presented in Table 4.12. The EDM construction cost for 78 stacks was \$7,800,000. The annual operating costs were \$241,000 for EDM electricity and \$517,000 for NaCl. The total present value cost was \$18,099,000. The unit treatment cost, comprising amortized capital cost and operating cost for electricity and NaCl was \$2.61 per thousand gallons of concentrate recovered or \$850 per acre-foot.

## **CHAPTER 5:**

# **Market Readiness Assessment**

EDM is a new technology that has yet to be implemented for continuous use at a treatment facility. To assess the market readiness of EDM for full-scale implementation, the research team considered the steps in the evolution of a new water treatment technology from conception to market readiness. In the research team's opinion, the following steps are typically required to bring a new water treatment technology to market:

- Develop the device concept.
- Conduct testing at bench- and pilot-scale.
- Use bench- and pilot-scale test results to evaluate the technical and economic feasibility of the device.
- Establish a structure for manufacture, distribution, startup, and training.
- Conduct a full-scale demonstration study.
- Evaluate the demonstration results and make improvements.
- Conduct another full-scale demonstration with the improved device and operating protocols.
- Manufacture the device for commercial application.

Our criteria for market readiness and our assessment of current EDM market readiness with respect to the criteria are shown in Figure 5.1 and discussed below.

### **5.1 Concept Development**

EDM was invented by Dr. Tom Davis, and the EDM concept was developed over several years of research and testing beginning in 2002. EDM was patented in 2008 (Patent No. 7,459,088). Dr. Davis has been an expert in the field of electrodialysis for almost 50 years. Electrodialysis has been practiced for over 50 years, and the principles and concepts are well understood. The research team concurs that the EDM concept conforms to electrodialysis principles and is theoretically sound.

### **5.2 Conduct Bench-scale and Pilot-scale Testing**

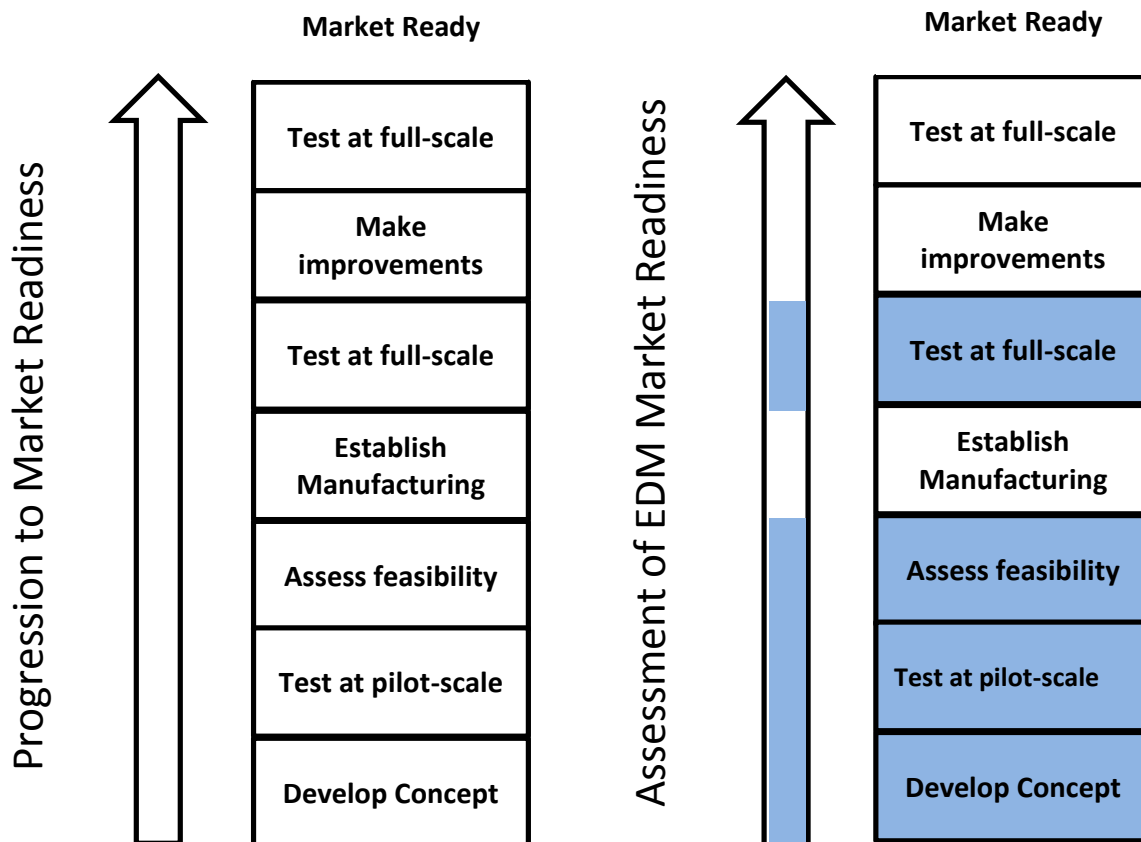
Extensive bench-scale and pilot-scale tests have been conducted with EDM. The following represents the chronology of EDM testing prior to the start of this project:

- Bench-scale evaluation of seawater desalination by Tom Davis at the University of South Carolina, 2002
- Pilot-scale treatment of irrigation return water by Tom Davis for the United States Bureau of Reclamation, 2006

- Pilot study by Tom Davis for El Paso Water Utilities, 2007
- Pilot study by Tom Davis for Sandia National Laboratories, 2007 - 2008
- Pilot-scale study conducted by Veolia and the University of Texas El Paso Center for Inland Desalination, 2007 – 2008
- Pilot-scale study conducted by this research team for the Water Research Foundation, 2010

This research team conducted the pilot-scale study in the last bullet above (Bond et al. 2010). Four different concentrate sources were tested with TDS concentrations ranging from 4,000 mg/L to 16,000 mg/L. There were, however, two essential differences between the pilot-scale EDM stack tested in 2010 and the full-scale stack tested in this study.

**Figure 5.1: Criteria for Market Readiness for a New Water Treatment Technology**



First, the membranes in the pilot-scale EDM stack were manufactured by Tokuyama Corporation and the membranes tested in this study were manufactured by Mega. Area resistance of the Mega membranes is approximately twice that of the Tokuyama membranes.

Second, in the pilot-scale stack, concentrate compartments were separated from sodium chloride compartments by monovalent selective membranes, but the EDM stack tested in the current study was not manufactured with monovalent ion-selective membranes. Monovalent membranes provide an additional level of protection against contamination of the concentrate streams from divalent ions present as impurities in the sodium chloride streams.

### **5.3 Evaluate Technical and Economic Feasibility**

In the study conducted by Bond and coworkers (2010), the research team concluded the pilot-scale EDM performed as intended in experiments treating four concentrate streams with a range of TDS concentrations from 4,000 mg/L to 16,000 mg/L. The research team projected full-scale costs and energy usage rates based on the pilot results. We compared the cost and energy consumption for treating EDM concentrate with the established technology, thermal desalination. For the brackish sources we tested, EDM was judged to be more than fifty percent less expensive and energy intensive. The research team concluded EDM was technically and economically feasible for recovering product water from concentrates generated desalinating brackish water sources.

### **5.4 Establish a Structure for Manufacture, Distribution, and Training**

In order for a utility to make a capital investment of millions of dollars to purchase water treatment equipment, the equipment must be backed by a manufacturer or vendor with the financial capability to provide solid equipment warranties and water quality performance guarantees. Such guarantees are particularly important for a new technology.

As an alternative to public ownership, a private company could own and operate an EDM concentrate treatment plant adjacent to the utility's desalination facility. In this scenario, the utility might pay the private company to accept the utility's concentrate, and the private company would be responsible for treatment of the concentrate and disposal of any waste products. The private company might sell guaranteed quality product water back to the utility.

Currently there appears to be no avenue to commercialization of EDM for public or private ownership. Veolia held an exclusive license to implement the EDM technology in North America for three years prior to 2014. The research team understands Veolia's plan was to act as the equipment vendor and have Mega manufacture the EDM stacks. Mega is a Czechoslovakian company that specializes in manufacture of ion exchange membranes and electrodialysis systems. In 2014, however, Veolia elected not to renew their EDM license.

At present, there are no entities designated to manufacture EDM or to act as the equipment vendor. Conceivably, an engineering firm could design and specify EDM equipment for a utility and have Mega or Tokuyama Corporation manufacture the stack, but in this scenario it is not clear if there would be a party responsible to the purchaser for equipment warranties and water quality performance guarantees.

Furthermore, it is unclear at this time who would provide EDM startup and training services. EDM has a higher level of process and operational complexity than typical water treatment equipment. Implementing EDM at a water treatment plant will require extensive training of the

utility's staff and a long startup period as the utility's staff transitions to operating EDM without assistance.

## **5.5 Conduct a Full-Scale Demonstration Study**

The research team conducted a full-scale demonstration of EDM treatment of RO concentrate at the BHWTF as reported. The full-scale demonstration reaffirmed the technical and economic feasibility of EDM for treating RO concentrate from a brackish water desalination facility. The full-scale test was also beneficial for illuminating areas where improvements might make operation and maintenance easier. The following are observations by the research team in that context.

### **5.5.1 Membrane Scaling**

The EDM stack that was delivered to the site for testing contained membranes that had been used previously at another site. High EDM diluate pressures indicated the membranes were scaled. Membrane scaling occurred again at the end of testing when the research team stopped operating the stack conservatively with respect to concentrate stream conductivities to determine how far recovery could be pushed. Inspection of the membranes showed scaling occurred in the mixed sodium concentrate compartment, and based on solubility limits the research team surmised the scale was from sodium sulfate and sodium bicarbonate. Continued testing should allow clear guidelines to be established for concentrate stream conductivities that minimize membrane scaling while optimizing EDM recovery by not using limits that are too conservative.

### **5.5.2 Membrane Clean in Place (CIP)**

As noted above, the EDM stack was delivered to the site with scaled membranes. Prior to testing two CIPs were performed according to the membrane manufacturer's recommendation, but neither was effective as indicated by continued high EDM diluate pressure. The research team took the stack apart, and the membranes were cleaned manually. This process required disconnecting all hoses, a forklift to lift the stack out and put it back in, and a full day of labor by two people to take the stack apart, clean the membranes, and reassemble the stack. The membranes became scaled again in the latter part of testing. A CIP was performed and again was ineffective. The manual cleaning process was repeated. It is the research team's opinion that taking the EDM stacks apart and manually cleaning the membranes will be required on a regular basis. Consequently, EDM plant design and staffing projections should be made with this maintenance requirement in mind.

### **5.5.3 Leakage between Compartments**

Early in the testing period, high sulfate concentrations were measured in the sodium chloride stream over a period of several days. This peak in sulfate concentrations caused a parallel peak in sulfate in the mixed chloride concentrate stream. Without leakage, sulfate concentrations should have been negligible in both streams. The research team surmised the sulfate contamination was caused by leakage between compartments, but we did not find a cause for the leakage. Sulfate concentrations dissipated to expected levels in both streams over the course of a few days, and the incident did not occur again.



Other than the sulfate peaks described above, the research team did not observe leakage between compartments, but EDM requires diligent maintenance during manual cleanings to avoid leakage between compartments. Based on the ineffectiveness of the several CIPs performed during testing, it is likely that EDM stacks in a full-scale plant would need to be taken apart on a regular basis and cleaned manually. An EDM stack with 120 quads contains over 480 membranes as well as mesh spacers between membranes. Each piece must be put back in the correct position to prevent leakage between compartments. The research team tightened the bolts holding the stack frame together each time the EDM stack was started. Failure to keep the stack frame at the minimum required compression could cause also leakage between compartments. EDM inherently contains twice as many membranes and compartments as conventional ED or EDR, and hence the potential for leakage between compartments is higher than for conventional ED. Furthermore, leakage between compartments in EDM has greater potential to cause membrane scaling because concentrations in the stack are so great. Nevertheless, it should be noted this scaling potential would be applicable to any treatment technology capable of treating RO concentrate with over 95 percent recovery.

## **5.6 Current State of EDM Market Readiness**

Sufficient bench-scale and pilot-scale testing has been conducted to confirm the technical and economic feasibility of EDM for treating RO concentrate from brackish water desalination facilities. An initial round of full-scale demonstration testing has been conducted to confirm the scalability of the EDM process from pilot-scale to full-scale. This testing was valuable for learning the treatment and recovery capabilities of the full-scale stack with Mega membranes, and it also helped identify some areas where improvements would enhance EDM productivity and usability. The next steps are to use the full-scale test results to make improvements and conduct another full-scale demonstration at a utility interested in implementing EDM.

The research team believes the following are either required or beneficial in completing the progression of EDM to a market ready water treatment technology:

- Establish the following regarding manufacture, distribution, training, and startup:
- Determine who will manufacture EDM for commercial use.
- Determine who will provide equipment warranty and water quality and energy consumption guarantees to potential purchasers.
- Determine who will market and sell EDM.
- Determine who will do operator training and plant startup.
- Use the full-scale test results to establish operating guidelines for critical parameters such as maximum current density and maximum concentrations in the concentrate streams to avoid membrane scaling.
- Consider any product improvements that can make cleaning and reassembling the EDM stack faster and easier, e.g., color coding of membranes.

- Consider any improvements that can be made to stack design that lessen the potential for membrane scaling.
- Consider any improvements that can be made to stack design that lessen the potential for leakage between compartments.
- Be prepared to provide a full-scale stack for testing and support to utilities interested in implementing EDM to demonstrate the performance of EDM treating their specific water source.

## CHAPTER 6:

### Recommendations to Utilities

There are many utilities in California as well as other regions of the U.S. with current or looming concentrate management challenges. The established method of treating desalination concentrate with thermal technologies is costly and massively energy intensive. The expense of established concentrate management methods has fostered a new wave of emerging technologies seeking to provide concentrate management at lower cost and energy expenditure.

Typically, innovation and solutions closely follow demand in the water industry. If the demand for affordable and sustainable concentrate management solutions continues to grow, it seems likely that one or more of the emerging concentrate management technologies will be on the market before 2020. Affordable solutions to concentrate management will open the door for utilities to expand their water supply portfolios to include greater use of brackish water sources.

The research team suggests the following factors to consider for a utility weighing the decision to pursue concentrate treatment with EDM or any other technology:

- Complexity of the treatment process. Concentrate treatment can be complex due to the difficulty of operating a single treatment process operators are unfamiliar with, by the number of treatment processes involved, or both. Concentrate treatment is inherently more complex than conventional water treatment because concentrations of contaminants that must be removed are four to five times greater.
- Staffing. The complexity of concentrate management may require a higher level of operator staffing than required for a similar capacity of RO membranes. For example, maintenance staff will be required for the labor intensive operation of manually cleaning EDM membranes and reassembling the stacks.
- Scale. Capacities of the concentrate treatment equipment are small in comparison to the rest of the treatment plant. Influent flow to EDM would typically be 15 to 25 percent of influent flow to the RO system, and EDM concentrate flow would be approximately 1 percent of the influent flow to the RO system.
- Sustainability. Regulations intended to protect our water resources and ensure conservative use of water and energy make sustainability an important consideration. Some questions to consider in this regard include the following:
  - What is the fate of the salts in concentrate?
  - How much energy does the concentrate treatment system use?
  - Will the concentrate management solution still be viable in one or two decades considering tightening environmental regulations and increased need for energy and water conservation?

- Will sewer discharge still be allowed in the future? If so, will the quantity or water quality limits change? Will the cost become prohibitive?

Among the emerging technologies for concentrate management, EDM offers two important advantages:

1. EDM is capable of directly treating RO concentrate at recoveries comparable to a thermal brine concentrator but using up to twenty times less energy than a thermal brine concentrator.
2. EDM presents the opportunity to use RO concentrate beneficially. In this demonstration EDM concentrate was treated to precipitate calcium carbonate and produce a sodium chloride-rich stream that could be recycled back to the EDM in lieu of purchasing the salt. This capability offers potential for lower treatment costs and a sustainable solution for managing the salt in RO concentrate.

In the current, changing landscape of water and energy use, prudent utilities are planning now for future needs, including the need to manage RO concentrate. Our test results with EDM indicate it is a promising solution for concentrate management. We recommend, however, that any utility considering EDM or any other emerging concentrate treatment technology conduct site-specific testing with the technology to obtain a full understanding of the complexity, viability, cost, staffing requirements, and sustainability of the process.

## CHAPTER 7:

### Benefit to California Ratepayers

There may be no region in the world where the interrelated and often competing challenges of water supply, energy consumption, and salinity management are more critical than in California. The ability to efficiently manage concentrated streams resulting from desalination, agricultural runoff, power plant cooling water, and industry is at the core of all of these issues.

The need for treating concentrated streams from drinking water desalination, water reclamation facilities, and power plants in California is critical and well documented. The following concerns were noted in the 2009 California Water Plan:

- Climate change is already having an impact on California water supplies and energy consumption.
- Operation of the water system to meet the needs of agriculture and domestic supply simultaneously will become increasingly difficult because of the tradeoffs that must be made.
- Water supply reliability will be compromised.
- Water should be used more efficiently with greater reuse and recycling.
- Energy consumption for water recovery should be reduced per unit of water recovered for reuse. This demonstration showed that Electrodialysis Metathesis successfully only used 0.6 kilowatt hours of energy per cubic meter of reverse osmosis concentrate treated (2.27 kilowatt hours per 1,000 gallons) and recovered 95 percent of the reverse osmosis concentrate as product water.

The following concentrate management issues were discussed in *The Southern California Regional Brine-Concentrate Management Study* (2009) conducted by the US Bureau of Reclamation:

- The management of desalination concentrate was identified as a significant issue in addressing southern California's water supply reliability.
- The study identified 199 wastewater facilities, 53 groundwater desalters, and 19 outfall systems that were expected to generate 47.4 mgd of concentrate in Southern California in 2010.
- Concentrate generation in southern California was projected to increase to over 135 mgd by 2035.
- RO systems are also used to remove the growing list of regulated contaminants, and regulatory changes could increase concentrate generation significantly beyond projections.
- Additional concentrate treatment will be needed.

Several California Energy Commission reports have addressed the water consumption, environmental, and energy issues associated with power plant cooling water reuse, e.g., *Issues and Environmental Impacts Associated with Once-Through Cooling at California's Coastal Power Plants* (2005) and *Cost and Value of Water Use at Combined-Cycle Power Plants* (2008). The proposed technology can reduce the cost and energy required to treat and reuse power plant cooling water.

There is an urgent need for salinity management in the agriculture industry in California. California is home to some of the most productive agricultural fields in the world, but increasing soil salinity is threatening continued agricultural use of large tracts of land in regions like the West San Joaquin Valley.

This project will benefit Californians because EDM has significant potential to address the issues of water and energy use and salinity management associated with desalination, water reclamation, power generation, and agricultural production in California.

## CHAPTER 8:

### Summary and Conclusions

The purpose of this project was to perform a full-scale demonstration of an emerging electro dialysis technology, EDM, for treatment of RO concentrate. The research team operated a full-scale EDM stack to treat RO concentrate generated at BHWTF from September 2013 through May 2014.

The overall project goal was to reduce the energy required to treat concentrated water streams. The solution investigated in this project has potential application to treat concentrate from desalting treatment plants, water reclamation facilities, agricultural runoff, and power plant cooling water.

Specific project objectives were to investigate the following during treatment of RO concentrate at the BHWTF:

- EDM energy requirements
- Resistance across the EDM stack
- EDM stack current utilization efficiency
- Limiting current density for the EDM system
- Separation of EDM concentrate into two streams of highly soluble salts
- Recovery achievable with EDM
- Rate of water transport with ions through EDM membranes
- Relative transport of ions through the EDM membranes.
- Treatment of EDM concentrate to recover sodium chloride and other salts.
- Optimal strategy for using EDM to reduce energy requirements and minimizes waste byproducts

Water quality of the RO concentrate varied during the study depending on which groundwater wells were in service. The average conductivity for the BHWTF RO concentrate was 4.1 mS/cm. The treatment goal was to produce EDM diluate with a conductivity of 1.8 mS/cm or less.

The research team concluded the following from test results with the full-scale EDM stack:

- EDM met the treatment goal using approximately 0.6 kWh/m<sup>3</sup> (2.27 kWh/kgal) of energy and with a recovery of 95.3 percent. The energy required for EDM was less than 5 percent of the energy required to achieve comparable recovery with a thermal brine concentrator, 20 kWh/m<sup>3</sup> (76 kWh/kgal).

- We observed no increase in resistance across the EDM stack over several months of operation until the end of testing when the membranes became scaled. This membrane scaling caused an increase in resistance.
- The current utilization calculated for the EDM stack ranged from 0.60 to 0.71. This is relatively low for electrodialysis. Improvements to the stack to increase current utilization would make the stack more energy efficient and more economical to operate.
- The limiting current density was determined for four diluate cell velocities: 5 cm/s, 6 cm/s, 7 cm/s, and 8 cm/s. These results were used to develop the relationship between cell velocity and the limiting polarization parameter that the research team used as a guide in testing and evaluating EDM. The relationship was  $P_{lim} = 207 v^{0.48}$ .
- Ions in the EDM diluate, sodium chloride, and concentrate streams were measured throughout testing to evaluate the separation of EDM concentrate into two streams of high solubility, one comprising mostly sodium and anions and the second comprising mostly chloride and cations. Separation of salts into two highly soluble concentrate streams is the key the EDM process. The research team concluded that EDM was effective in separating salts into two highly soluble concentrate streams as intended.
- Recovery for EDM depends on water quality of the feed water and the number of equivalents removed during treatment. Water is transported from the diluate to the concentrate compartments with the passage of ions through the membranes. EDM recovery of feed water (BHWTF RO concentrate) was 99 percent. Dilution water, however, in the form of RO permeate was added to the EDM concentrate streams to maintain conductivities below 50 mS/cm in the mixed sodium concentrate and below 150 mS/cm in the mixed chloride concentrate. Use of RO permeate as dilution water would reduce the overall plant production, and therefore the research team accounted for this loss in calculating EDM recovery. Accounting for the loss of dilution water reduced EDM recovery to 95 percent.
- The rate of water transport through membranes into the concentrate compartments establishes the maximum recovery levels that can be achieved with EDM. The research team measured the rate of water passage through the membranes at several points during testing. Water transport was consistently around 20 moles per eq of charge transported for each concentrate stream. Varying the concentration of the sodium chloride stream did not affect the water transport rate.
- The research team measured ions in the EDM streams and performed mass balance calculations to determine RTNs of the counterions. The RTNs for Ca:Na and Mg:Na were similar, approximately 2.0. The RTNs for SO<sub>4</sub>:Cl and HCO<sub>3</sub>:Cl were similar, approximately 0.5.



- The research team evaluated a two-step process for treating EDM concentrate to recover salt and sodium chloride. EDM consumes sodium chloride during treatment, and the consumed NaCl ends up in the two EDM concentrate streams. The cost to purchase NaCl represents a greater operating cost than the energy used. The prime objective of this experiment was to determine if NaCl could be recovered from EDM concentrate as a means to reduce the cost for EDM treatment. In the first step, we blended the two EDM concentrate streams and precipitated  $\text{CaCO}_3$ . At the end of this precipitation step, the resulting supernatant was 84 percent NaCl. The supernatant was fed to an ED stack containing monovalent selective membranes, where the objective was to selectively remove and concentrate NaCl. The ED concentrate reached a conductivity of 195 mS/cm, near the saturation level of NaCl. At the end of treatment with ED, the ED concentrate was 97 percent NaCl. The research team concluded this two-step process was effective for the recovery of sodium chloride.

Following testing, the research team used the test results to evaluate full-scale application of EDM for concentrate treatment at plants operated by the city of Beverly Hills, Rancho Water District of California, and the city of Santa Monica. The objective was to investigate optimal strategies for minimizing treatment costs and energy consumption with EDM. This evaluation also demonstrated the applicability of EDM for different water sources and different treatment goals.

The Beverly Hills and Santa Monica plants desalinate groundwater to produce drinking water. The Rancho Water District plant is a water reclamation facility. For the Beverly Hills and Santa Monica plants, we performed the analyses assuming ED diluate would be blended with RO permeate, and the EDM treatment goal was based on meeting a blended product water TDS. For the RWD evaluation, we assumed the ED diluate would be blended with the RO feed, and the treatment goal was to produce ED diluate with the same conductivity as the RO feed noting additional intermediate treatment would be needed for silica and TOC removals.

The costs we included in the analyses were installed cost for EDM and operating costs for energy and purchase of NaCl. These costs do not represent the full costs that would be estimated during detailed engineering design and would be site specific. For example, some utilities might have room for EDM in the existing RO building while others would require a new building. The intent of our evaluation was not to capture such costs but rather to present costs for EDM alone.

The research team evaluated the effect of mode of operation on treatment costs and energy consumption. The modes of operation we evaluated were 1-stage EDM, 2-stage EDM, and 3-stage EDM treatment. Recirculation of EDM diluate was used for each mode as necessary. The research team also evaluated the effect of cell velocity on cost and energy consumption. Forty percent more stacks than required by capacity were used in the capital cost calculation. This redundancy was built into the design to account for stack down time for cleaning.

In some cases, polarization parameter rather than cost determined which mode of operation or cell velocity was selected to represent treatment cost. For example, there were cases where operating at a higher velocity or greater reduction in conductivity per stage resulted in lower cost but a smaller factor of safety with respect to the limiting polarization parameter. In such cases, the research team selected the next least expensive mode of operation with the greater polarization parameter safety factor. No costs were reported for modes of operation where the polarization parameter exceeded 80 percent of the limiting value, and we typically selected options with PP values in the range of 50 to 60 percent of the limiting value to allow operational flexibility.

The results of our evaluation of EDM treatment of RO concentrate at the three plants are as follows:

- NaCl consumption and cost were the same for each mode of operation because the same number of equivalents is removed by EDM to meet the treatment goal regardless of the number of stacks in series or the amount of diluate recirculation.
- The cost for NaCl consumption was greater than the cost for EDM electricity.
- Costs decreased as cell velocity increased, but the polarization parameter increased. We generally found that a cell velocity of 5 cm/S provided comparable treatment cost to higher velocities but with a better polarization parameter safety margin.
- Treatment costs increased as the reduction in RO concentrate conductivity required increased.
- For Beverly Hills, a 56 percent reduction in RO conductivity by EDM was required to meet the treatment goal.
- A recycle ratio of 1.0 was required to achieve the treatment goal with one EDM stage. No recycle was required for two-stage or three-stage treatment.
- The cost for one-stage operation and two-stage operation were essentially identical and less than three-stage operation.
- Treatment cost was 7 percent less at a cell velocity of 6 cm/s than at a cell velocity 5 cm/s. Polarization parameter values exceeded 80 percent of the limiting value at cell velocities of 7 cm/s and 8 cm/s. A cell velocity of 5 cm/s was selected for the evaluation to provide greater polarization parameter safety factor.
- The treatment cost for EDM operating with two stages at a velocity of 5 cm/s was \$0.60/m<sup>3</sup> (\$2.28/kgal). The capital cost comprised 56 percent of the total and operating cost 44 percent (32 percent NaCl and 14 percent energy).
- Energy consumption for EDM was 0.6 kWh/m<sup>3</sup> (2.2 kWh/kgal).
- For RWD, an 82 percent reduction in RO conductivity by EDM was required to meet the treatment goal.

- A recycle ratio of 4.3 was required to achieve the treatment goal with one EDM stage.
- A recycle ratio of 1.0 was required to achieve the treatment goal with one EDM stage.
- No recycle was required for three-stage treatment.
- Three stage operation was least expensive.
- Treatment costs were equivalent at cell velocities of 5 cm/s and 6 cm/s. Polarization parameter values exceeded 80 percent of the limiting value at cell velocities of 7 cm/s and 8 cm/s. A cell velocity of 5 cm/s was selected for the evaluation to provide greater polarization parameter safety factor.
- The treatment cost for EDM operating with three stages at a velocity of 5 cm/s was \$1.18/m<sup>3</sup> (\$4.48/kgal). The capital cost comprised 43 percent of the total and operating cost 57 percent (38 percent NaCl and 19 percent energy).
- Energy consumption for EDM was 1.9 kWh/m<sup>3</sup> (7.2 kWh/kgal).
- For Santa Monica, a 56 percent reduction in RO conductivity by EDM was required to meet the treatment goal.
- A recycle ratio of 0.75 was required to achieve the treatment goal with one EDM stage. No recycle was required for two-stage or three-stage treatment.
- The cost for one-stage operation was approximately 4 percent less than for two-stage operation. Three-stage operation was more expensive than two-stage.
- Polarization parameter was at a safer level for two-stage operation than for one-stage. Consequently, two-stage operation was selected for the evaluation.
- Treatment cost decreased as cell velocity increased, but the cost differential decreased with each step up in velocity. For example, cost for 6 cm/s was 10 percent less the cost at 5 cm/s, but the cost at 8 cm/s was only 1 percent less than at 7 cm/s. The ratio PP/PPlim was 0.67 at 7 cm/s and 0.72 at 8 cm/s. A cell velocity of 7 cm/s was selected for the evaluation to provide greater polarization parameter safety factor.
- The treatment cost for EDM operating with two stages at a velocity of 7 cm/s was \$0.66/m<sup>3</sup> (\$2.49/kgal). The capital cost comprised 37 percent of the total and operating cost 63 percent (41 percent NaCl and 22 percent energy).
- Energy consumption for EDM was 1.2 kWh/m<sup>3</sup> (4.6 kWh/kgal).

## GLOSSARY

Term	Definition
a	ion activity
A	amperes
$A_m$	membrane cross-sectional area
AWTP	Arcadia Water Treatment Plant
BDL	below method detection limit
BHWTF	Beverly Hills Water Treatment Facility
C	molar concentration
°C	Degrees Centigrade
$\text{CaCl}_2$	calcium chloride
$\text{CaCO}_3$	calcium carbonate
$\text{CaMg}(\text{CO}_3)$	dolomite
$\text{CaSO}_4$	calcium sulfate
CIP	clean in place
cm/s	centimeters per second
DI	?
ED	electrodialysis
EDM	electrodialysis metathesis
EDR	electrodialysis reversal
F	Faraday's constant
GAC	granular activated carbon
gpm	gallons per minute
HMI	human-machine interface
I	current
i	current density
$I_{\text{actual}}$	actual current
$i_{\text{lim}}$	limiting current density
$I_{\text{theory}}$	theoretical current
J	ion flux
k	specific conductance (conductivity)
kg/d	kilograms per day
$\text{kWh/m}^3$	kilowatt hours per cubic meter
$\lambda$	moles/eq water transport rate
L	distance
$L_c$	concentrate flow rate
[Mg]	molar concentration of magnesium ions
$\text{MgCl}_2$	magnesium chloride
mgd	million gallons per day

mg/l	milligrams per liter
Mg(OH) <sub>2</sub>	magnesite
MINTEQ	?
mL	milliliter
MVC	mechanical vapor compression
μm	micrometer
μS/cm	microSiemens per centimeter
N	normality
Na	EDM dilute normality
Na	sodium
[Na]	molar concentration of sodium ions
NaCl	sodium chloride
Na <sub>2</sub> HCO <sub>3</sub>	sodium hypochlorite
NaOCl	sodium bicarbonate
NaOH	sodium hydroxide
Na <sub>2</sub> CO <sub>3</sub>	sodium carbonate
Na <sub>2</sub> SO <sub>4</sub>	sodium sulfate
N <sub>m</sub>	log mean normality
Ω/cm <sup>2</sup>	Resistance in ohms per square centimeter
p	Pressure
PIER	Public Interest Energy Research
PLC	programmable logic controller
PP	polarization parameter
PP <sub>lim</sub>	limiting polarization parameter
q	flow
q <sub>c</sub>	concentrate flow rate
q <sub>f</sub>	EDM flow rate
R	universal gas constant
R	resistance
r	area resistance
RCWD	Rancho County Water District
RD&D	research, development, and demonstration
RO	reverse osmosis
RTN	Relative Transport Number
SiO <sub>2</sub>	silica
SRWRF	Santa Rosa Water Reclamation Facility
SS <sub>res</sub>	sum of squared deviation from regression line
SS <sub>tot</sub>	sum of squared deviations from the mean
T	absolute temperature
t	transport number

$t_c$	time required to collect concentrate
TDS	total dissolved solids
Ti/Pt	titanium/plutonium anode
U	Electrical potential
u	mobility
v	cell velocity
V	partial molar volume
V	volts
v	stoichiometric coefficient
$v_c$	volume of concentrate collected
x	distance in the direction of diffusion
z	ionic charge
ZLD	zero liquid discharge
$\beta$	shadow factor
$\eta$	electrochemical potential
$\Lambda$	equivalent conductance
$\mu$	chemical potential
$\xi$	current utilization

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